A Study of the Vapour-Phase Catalytic Oxidation of o-Xylene

by

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SUMMARY

The catalytic vapour-phase oxidation of o-xylene has been studied in a stirred catalytic reactor, in a two inch i.d. fixed-bed reactor, and in a two inch i.d. fluidised-bed reactor, using the same commercial catalyst (promoted V_2O_5 on SiC) in each.

The operating conditions of the reactors are summarised below:

	o-Xylene Conc.	Oxygen Conc.	Temperature
Spinning Basket	0.1 - 0.3%	10 - 30%	391, 399, 411, 432°C
Fixed-Bed Reactor	0.5, 1.0%(inlet)	Air	370 - 480°C (wall)
Fluid-Bed Reactor	0.4, 0.8, 2.0 (")	Air	400 - 520°C

The kinetics of the oxidation of o-xylene were studied in the spinning catalyst-basket reactor. The main organic product was phthalic anhydride; small amounts of o-tolualdehyde and phthalide were also produced. It was demonstrated that homogeneous combustion of phthalic anhydride occurred to a significant extent at the residence times made necessary by the design of the reactor, but it was shown that o-xylene did not undergo homogeneous reaction under the same conditions. It was thus possible to measure the catalytic rate of o-xylene disappearance but the rates of the catalytic combustion of reactant and products were inaccessible. The experimental data were found to be adequately correlated by a rate law, first order o-xylene, zero order in oxygen:

$$R_X = k\, p_X$$

where $k = 6.27 \times 10^7\, e^{\frac{-26300}{RT}}$ (gm.moles/gmcat hr. atm)

A reversible deactivation of the catalyst was observed at xylene partial pressures above 0.016 atm., and eight experimental runs were found to have abnormally high rates of o-xylene disappearance. It is suggested that these two phenomena may be caused by changes in the catalyst oxide.

Several experiments using different catalysts were performed, but the results were limited and inconclusive.

The fixed-bed experiments were conducted under highly non-isothermal conditions (peak temperatures of up to 170° above the wall temperature) and at low Reynolds numbers (<20). An almost constant selectivity to phthalic anhydride of (approximately) 65% was observed at wall temperatures of 390°C to 440°C at residence times within the catalyst bed of less than a second. At longer residence times and higher wall temperatures a decrease in selectivity occurred, believed to be caused by homogeneous combustion of phthalic anhydride. The behaviour of the fixed-bed reactor is compared to that observed by Caldwell in his study of o-xylene oxidation in a one inch i.d. fixed-bed reactor operated at commercial flows.

The fluidised-bed experiments were conducted using the same catalyst but crushed to a size suitable for fluidisation. The observed selectivity to phthalic anhydride was virtually constant (at 50%) at temperatures below 500°C, but above this value a decrease was apparent. The fluid-bed catalyst exhibited a level of activity considerably below that expected from the spinning-basket results. Possible causes of the lower selectivity and activity are discussed.

The applicability to the "American" type catalyst of Froment's simplified reaction scheme (said to be representative of the industrial reaction over the "German" type of catalyst) is discussed. It is concluded that his scheme can be used to explain the results from the three reactors if it is assumed that the combustion of phthalic anhydride is largely homogeneous.

Errata

Page

8 - para 3, line 4 - "Benllock" should read "Benlloch"

25 - para 2, line 3 - "vanaduim" should read "vanadium"

35 - sect. 2.1.5, line 1 - "catalysts" should read "catalyst"

39 - para 3, line 2 - "anbydride" should read "anhydride"

46 - sect. 2.3.1, line 10 - "couple" should read "coupled"

119 - 2nd last line - should read "rate of o-xylene disappearance"

121 - 2nd last line - "independant" should read "independent"

Equations (1.5), (1.6), p 15)
(4.4), p. 79) - Redox equation - "K_X" should read "k_X"

The author apologises for these errors.

CONTENTS

Chapter 1

The Catalytic Oxidation of O-Xylene to Phthalic Anhydride

1.1 Introduction

Phthalic anhydride is one of the most important organic chemical intermediates. World production has increased from 700,000 tons/a. in 1960 to approximately 1.3 million tons/a. in 1969[1]; demand is expected to grow at a rate of slightly over 10% per annum[1,2]. The end use market distribution for phthalic anhydride was, in 1968, approximately as follows[3]:

Alkyds	27%
Plasticisers	55%
Polyesters	9%
Misc. (e.g. dyestuffs, pharmaceuticals etc.)	9%

Until recently, production had never succeeded in remaining ahead of demand for any length of time, but it has been suggested by Allen[2] that the present over-capacity is likely to continue (and probably increase) for several years. The highly competitive and growing market for phthalic anhydride has stimulated considerable research into the development of more efficient processes and catalysts.

1.2 History of Commercial Processes for Phthalic Anhydride Manufacture

Prior to 1920 phthalic anhydride was produced by the liquid phase oxidation of naphthalene. The early oxidising agents employed were usually nitric acid or chromic acid, but a more commercially viable process was patented by B.A.S.F. in Germany in 1896, in which the naphthalene was oxidised by sulphuric acid in the presence of mercury salts.

The yield of phthalic anhydride was only 25% of the theoretical value [4].

During the First World War, processes for the fixed-bed catalytic vapour-phase air oxidation of naphthalene, achieving 80% (approximately) of the theoretical yield, were developed independently in Germany and the U.S.A., resulting in patents by Wohl [5] in Germany and by Gibbs and Conover [6,7] in the U.S. The processes developed from these are essentially the same differing mainly in the mode of operation of the reactor and the temperature range of the catalysts, which are still described today as being of the "German" or of the "American" type.

In 1945, the Sherwin-Williams Co., of Chicago built the first fluidised-bed plant for the production of phthalic anhydride from naphthalene, but the catalysts employed in the early plants were sulphur-sensitive and suffered rapid attrition[8]. An improved catalyst[9] was introduced in 1959 by the United Coke and Chemicals Co., Ltd., and this catalyst is now used in virtually all the fluidised-bed plants operating today.

Prior to about 1940, all commercial production of phthalic anhydride was from naphthalene, originally obtained solely from coal tar distillation. The contraction of the coal gasification industry was accompanied by the increasing availability of naphthalene from petrochemical sources. The high price of petrochemical naphthalene stimulated development work to produce catalysts which would convert the more freely available ortho-xylene to phthalic anhydride by processes essentially similar to naphthalene oxidation. Today it appears that o-xylene has largely superseded naphthalene as the raw material in new plants[1,2]. The demand for o-xylene for other uses has risen rapidly in recent years, principally due to the growth of the use of the xylenes as petrol additives and the growth of the use of para-xylene in the manufacture of synthetic fibres, which has led to the development of processes to isomerise o-xylene to p-xylene.

The resultant uncertainty in feedstock supply has led to the development of processes and catalysts capable of operating on either naphthalene or o-xylene.

The processes currently available for phthalic anhydride manufacture are reviewed by Leach[3], and can be grouped into four classes:

a) Low space velocity fixed bed vapour phase processes

b) High space velocity fixed bed vapour phase processes

c) Fluidised bed vapour phase processes

d) Liquid phase process

1.2.1 Low Space Velocity Fixed Bed Processes

Most of the phthalic anhydride capacity installed recently belongs to this category. The catalyst employed is of the 'German' type; it consists of vanadium pentoxide on silica with potassium promoters[10, 11]. It is relatively mild and functions generally at temperatures in the range 350° - 410°C[3]. An o-xylene feed of about 0.78% (mole) in air is used, giving yields of phthalic anhydride of 69 - 75 mole%[1, 3]. Froment[12] gives data which he believes to be fairly representative of industrial practice with the German type catalyst, and which gives a space velocity of about 1200 per hour. A less recent publication[4] quotes contact times of 4 - 5 seconds for the low space velocity process against 0.4 - 0.6 seconds for the high space velocity process.

1.2.2 High Space Velocity Fixed Bed Process

This type of process employs an 'American' type catalyst of high activity and an operating range of 450 - 510°C[3].

The catalyst is again vanadium pentoxide but supported this time usually on alundum or carborundum[10]. Because of its high activity, this type of catalyst tends to give a lower measure of reaction control than the German type, which in time leads to higher by-product formation and lower yields. Typically, a feed concentration of o-xylene of about 1.4 - 1.6% is used and yields in the range 60 - 71 mole% are obtained[3]. Some high space velocity processes appear to operate inside the explosive limits for o-xylene in air, variously quoted as 1.0 - 5.3[13] and 1.1 - 7.0 mole%[14].

1.2.3 Fluidised Bed Processes

This type of process appears still to be confined to the use of naphthalene as feedstock. The catalyst employed is the U.C.C. catalyst[9], consisting of V_2O_5 and $K_2S_2O_7$ on silica. Air to naphthalene weight ratios of the order of 10:1 are used. Although these are well inside the explosive limits, it is claimed[3] that the catalyst particles tend to suppress any fast moving flame front and thus inhibit explosions. Yields from this type of process vary from 76 - 82 mole%[3, 8] depending on the quality of the naphthalene feedstock.

Until recently, the yields claimed for catalysts for use in fluidised-beds with o-xylene were only 57 - 61 mole%[15, 16]. Yields of up to 74 mole% have been reported[20] using a V_2O_5 - K_2So_4 - TiO_2 catalyst, and an improvement in the yield from 50 - 70 mole% has been reported[21] to have been achieved by the addition of 0.3% $B(O\,Et)_3$, or $B(OBu)_3$. The yield can also be raised by the addition of small amounts of bromine[17], and this has been developed in a recent U.S. patent[18] where the use of bromine is linked to the use of catalysts of the U.C.C. type; yields in the range 68 - 82 mole% are claimed at air to xylene weight ratios of 12:1.

The commercial development of this process will have to overcome the obvious problems of corrosion, bromine recovery and product loss by bromination.

One fluidised-bed plant using the o-xylene - bromine technique was built in the U.S., but closed down after only about one year's operation, reportedly[19] because of technical problems. It is of interest to note that the next phthalic anhydride plant ordered by the same company was based on a low space velocity fixed bed process.

The fluidised plant offers many advantages over its rival fixed-bed process:

a) because of its higher hydrocarbon:air ratio, for the same production rate of phthalic anhydride, the fluid-bed plant requires units of much smaller capacity, with a consequent reduction in capital and operating costs.

b) the fluid-bed reactor is simpler to construct.

c) in the fluid-bed process, because of the higher phthalic anhydride reactor exit concentration, it is possible to use liquid condensers (under pressure) which prevent the build-up of polymeric tars that occur in the solid condensers of the fixed-bed process.

d) the reactor offers better temperature control, and safer operation because of the suppression of homogeneous combustion.

Because of these and the uncertain feedstock supply position already discussed, there is still considerable desire for a successful fluid-bed xylene process.

1.2.4 Liquid Phase Process

There is little information available about this process (the French Progil process), but it has been reported[3,11] that the o-xylene is dissolved in acetic acid and oxidised by air in the presence of a cobalt acetate catalyst with a metal bromide promoter. The oxidation occurs at temperatures between 100°C and 275°C and at pressures up to 1500 p.s.i. Yields of up to 92% of the theoretical value are claimed. It is believed that very high purity xylene is required as feedstock.

1.2.5 Sulphur Dioxide Addition

In some of the phthalic anhydride fixed-bed processes, an addition of small quantities of sulphur dioxide is made to the gases prior to entering the reactor. The data in the original patent[22] make it clear that it was applied to a high space velocity process. It was claimed that the addition of sulphur dioxide resulted in a smoother reactor temperature profile, with a reduced peak and an increased bed average temperature. Two benefits were claimed for this:

a) the reduction of the "hot spot" temperature prevented catalyst and reactor damage and reduced the complete oxidation reactions.

b) or, a greater throughput could be achieved before the maximum tolerable temperature was reached.

The purpose of the sulphur dioxide addition to some low space velocity processes is principally to maintain catalyst activity[1, 11]. The quantity added is reported as 0.1 - 0.2% of the feed mixture[1].

1.3 Reaction Products and Kinetics

Table 1.1 gives a list of experimental laboratory studies of O-xylene oxidation conducted since 1939.

Table 1.1

Experimental Studies

Investigator	Year	Reactor	Catalyst	Temp. Range	Concentrations O_2	Xyl.	Major Products	Contact Time
arks/Allard (23)	1939	Fixed-bed	V_2O_5	450-530°C	Air	0.4-9.0%	PA, TA, CO_2	<0.5 secs
imard et al (24)	1955	Fixed	V_2O_5/SiC	460	Nitrogen, Air	1.1,3.3%	PA, MA, COX	0.26
imard (unpubl) (25)	?	Fixed	V_2O_5/SiC	400 - 450	Air	0.4-1.4%	PA, TA, MA, COX	0.01-0.06
hattacharyya and ulati (26)	1958	Fixed	Fused V_2O_5	360 - 480	Air, Oxygen	0.2-0.4%	PA, MA, CO_2	0.6
ovella/Benlloch 35, 36, 37)	1962	Fluid	V_2O_5/K_2SO_4 on SiC	310 - 370	Air	1.1,1.5,2.5%	PA, MA, TA, COX	20
hallacharyya and rishnamurthy (27)	1963	Fluid	Fused V_2O_5	490	Air	1.05%	PA, TA, CO_2	0.4
arra/Beltrame(33)	1964	Fluid	V_2O_5 on SiO_2	410, 460	Air	0.25-1.1%	PA, MA, CO_2	< 10
liev (34)	1965	Fluid	"KO-33"	380 - 420	Air	0.5-1.5%	PA, MA, CO_2	?
ernardini/Ramacci 32)	1966	Fixed	V_2O_5 on corundum	450 - 500	Air	0.8-1.3%	PA, MA, TA, PI COX	0.07
bo et al (20)	1967	Fixed	V_2O_5/K_2SO_4/	340	Air	0.8%	PA, MA, COX	
"	"	Fluid	TiO_2	370 - 410	Air	0.8%	PA, MA, COX	0.15-0.75
erten/Froment 38)	1968	Fixed	"Synoxy"	325-402	10-100%	0.5-2%	PA, PI, TA, COX	1
ann/Downie (39)	1968	Fixed	V_2O_5/K_2SO_4	300-325	6-50%	0.7-3%	PA, TA, PI, COX p-benzoquinone	0.1
uusola/Mann/Downie 41)	1970	Fixed	"	290-310	3-50%	0.3-1.5%	TA(80%)COX p-benzoquinone	?
aldwell (30)	1971	Fixed	V_2O_5/SiC	370-520	Air	0.5,1.0%	PA, PI, CO_2	1

The literature prior to this date has been reviewed by Parks and Allard[23], and consists mainly of preliminary results of searches for selective catalysts. Both the 'German' and the 'American' types of catalyst are well represented in these studies.

Parks and Allard[23] found that, at low air:xylene ratios, tolualdehyde could be produced exclusively, whereas high ratios favoured phthalic anhydride. Simard et al[25], in an unpublished investigation, limited conversions to below 25% and obtained tolualdehyde yields of 10 - 40%. Mann and Downie[39] and Juusola, Mann and Downie[41] limited their conversion, the latter to 6% where they obtained tolualdehyde selectivities of 80%. With these exceptions, the maximum yields of phthalic anhydride reported are in the range 50 - 72%, comparable with industrial yields.

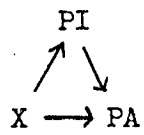
As can be seen in Table 1.1, while the inlet xylene concentration has been varied extensively in these studies, the majority of workers have used air throughout, thereby giving no information on the oxygen dependency of the reaction rates. The more recent studies in which the oxygen concentration has been varied - viz. references 38, 39, 41 - have employed the 'German' type of catalyst. A notable exception is the work of Bhattacharyya and Gulati[26] who report virtually no difference in product distribution or total conversion on a fused V_2O_5 - pumice catalyst at 490 - 540°C when they changed from an oxygen:xylene molar ratio of 20:1 to a ratio of 85:1, achieved by changing the oxygen concentration.

Several reaction schemes have been proposed for o-xylene oxidation and these are shown in Figure 1.1. The orders of reaction and activation energies associated with some of these shemes are given in Table 1.2.

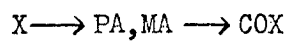
Bernardini and Rumacci[32] succeeded in oxidising phthalide, o-toluic acid, o-tolualdehyde and o-methylbenzyl alcohol to phthalic anhydride with selectivities of greater than 85%.

FIGURE 1.1 - REACTION SCHEMES

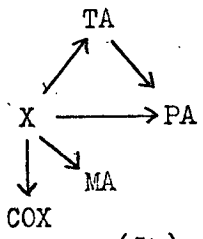
a) Levine (simplified) (55)



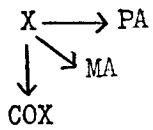
b) Carra,Beltrame (33)



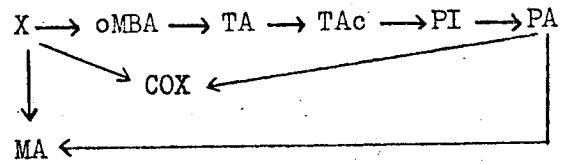
c) Simard (25)



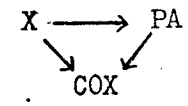
d) Aliev (34)



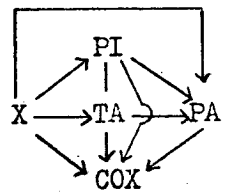
e) Bernardini,Ramacci (simplified) (32)



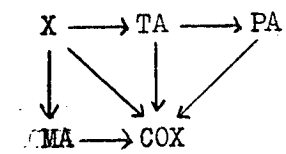
f) FROMENT (12)



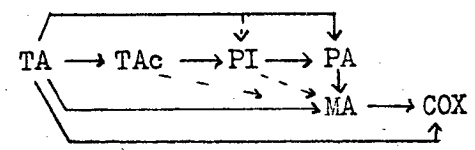
g) Herten,Froment (38)



h) Novella,Benlloch (35-37)



i) Vrbaski,Matthews (42)



(— well established)
(-- probable)

Table 1.2

Orders of Reaction and Activation Energies

Key - column a - order re hydrocarbon

" b - order re oxygen

" c - activation energy (k cal/mole)

k	Reaction	Simard		Novella		Carra		Aliev		Froment		
		a	b	a	c	a	c	a	c	a	b	c
	X disapp			1	15	0.5	31					
	X to TA	1	0.5	1	9							
	X to PA	0	0.5	-				1	15	1	1	27
	X to MA	0	0.5	1	5			0.5	14			
	X to COX	0	0.5	1	23			1	17	1	1	29
	TA to PA	1	0.5	1	11							
	TA to COX			1	19							
	PA to COX			1	25	1	32			1	1	31
	MA to COX			1	18	1	32					

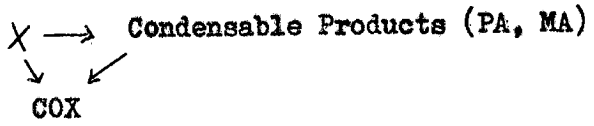
Note References (38), (39), (41) report varying orders of reaction; all correlated their results via a Redox model. They are discussed in Chapter 4.

Their maximum selectivity when they commenced with xylene was only 65%. Vrbaski[56] and Vrbaski and Matthews[42] have deduced a similar scheme from their studies of the oxidation of o-methylbenzyl alcohol and o-tolualdehyde respectively.

Three schemes propose a parallel formation of phthalic anhydride directly from xylene and via tolualdehyde. None of them, however, produce any kinetic data from which the relative importance of each of the parallel routes may be gauged.

Apart from tolualdehyde, the major isolatable organic byproduct occurring in the majority of these schemes is maleic anhydride, which is shown as being formed, in part at least, directly from o-xylene. In their study, Novella and Benllock found that phthalic anhydride could not be oxidised to maleic anhydride in their operating range of 310 - 370°C, and so concluded that maleic anhydride was formed only from xylene. Bernardini and Ramacci, however, found that while no maleic anhydride was obtained from phthalic anhydride oxidation at 360°C, substantial quantities resulted when the oxidation was conducted at 500°C. The apparent conflict in the mode of maleic anhydride formation may be resolved by the conclusion that at low temperatures (typical of a 'German' catalyst) phthalic anhydride does not combust to maleic anhydride while it does at the high temperatures typical of the 'American'catalyst.

Apart from Levine's scheme which ignores carbon oxides formation, the only scheme which does not have direct xylene combustion is that of Carra and Beltrame. These workers correlated their data using a triangular scheme:



They obtained the best correlation, with the orders given in Table 1.2, when the xylene combustion step was of virtually zero magnitude. The reasons for their assumption that the maleic and phthalic anhydride concentrations might be summed and treated as one, thereby ascribing the same orders of reaction to their formation and to their combustion, are not clear. The orders assigned to the formation reactions of phthalic anhydride and maleic anhydride by both Simard[25] and by Aliev[34] are different from each other, while Volfson et al[57] concluded that phthalic anhydride oxidation proceeded by two parallel routes, one to maleic anhydride, the other to carbon oxides.

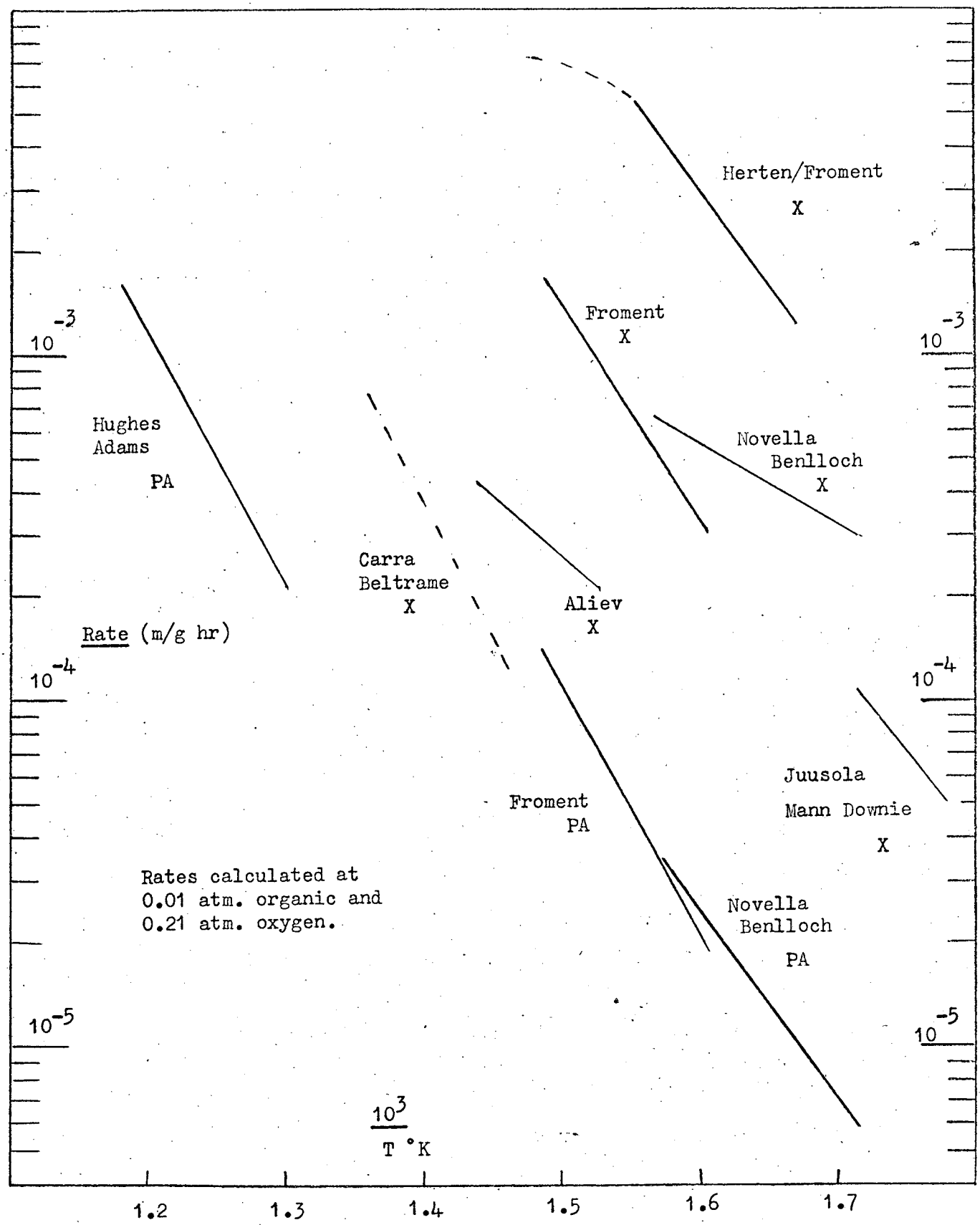
The complete combustion reactions are of considerable importance since their occurrence limits the attainable selectivity to phthalic anhydride and since the large heat release from these reactions constitutes a major reactor design problem.

While most of the schemes in Figure 1.1 indicate that virtually all of the organic compounds may be oxidised to carbon oxides, information on the relative rates is generally lacking. Bernardini and Ramacci[32] concluded that the oxidation of phthalic anhydride was inhibited by the presence of xylene and intermediates since they found that pure phthalic anhydride was readily oxidised under the conditions used for its production from xylene. While Herten and Froment[38] state that "with excessive residence times the decomposition of PA into Co and Co_2 is beyond doubt and was easily proved" their results show no sign of a maximum in the phthalic anhydride yield as complete xylene conversion is approached, suggesting that the rate of phthalic anhydride oxidation is "normally" small.

Froment[12] provides data for his scheme, said to be representative of the industrial air oxidation of xylene over the 'German' catalyst. Novella and Benlloch[35-37] and Carra and Beltrame[33] provide kinetic data for each step in their schemes, while Aliev[34] gives activation energies for his. Herten and Froment[38], Mann and Downie[39], and Juusola, Mann and Downie[41] provide data for the total xylene disappearance rate only. These various rates of xylene disappearance and of phthalic anhydride oxidation are presented graphically in Figure 1.2. The results of Hughes and Adams[29] study of phthalic anhydride oxidation on a V_2O_5/SiC catalyst are included.

In their study, Carra and Beltrame used a contact time defined as the mass of catalyst divided by the mass flow of gas, resulting in values of the order of 1000 seconds. This same time base appears in their kinetic parameter values. Using values quoted in their paper for catalyst mass and density, bed voidage and for typical flowrates, a more realistic contact time (defined as volume of catalyst bed divided by volume flowrate at reaction temperature) of approximately one second may be calculated. Consequently, their stated kinetic parameters have been multiplied by 1000 before plotting their rates in Figure 1.2, and should be considered as approximate values only. Their relative rates of phthalic anhydride oxidation and xylene oxidation are unaffected since they used the same time base in each. At the same concentration of organic reagent, their rates of phthalic anhydride oxidation are approximately four times greater than their rates of xylene oxidation. Carra and Beltrame are the only workers to have found a greater rate of phthalic anhydride oxidation, and theirs is the only scheme which does not have a direct xylene combustion step.

FIGURE 1.2 - RATES of REACTION of o-XYLENE (X) and PHTHALIC ANHYDRIDE (PA) on V_2O_5 CATALYSTS



The activation energies for o-xylene disappearance and phthalic anhydride oxidation are generally in the range 25-30 k cal/mole; Novella and Benlloch report a lower value of 15.4, similar to that of Aliev.

Novella and Benlloch, and Froment present data for both the rate of xylene disappearance and phthalic anhydride oxidation. In both cases, although the activation energies for the latter reaction are the greater, the rate of phthalic anhydride oxidation, at the same concentration of the organic and oxygen, is less than one-tenth of the rate of xylene disappearance. In view of the fact that industrial yields are in the range 60-70%, these relative rates suggest that a scheme of xylene → phthalic anhydride → carbon oxides is not adequate. Since relatively small amounts of other organic products are found, and because of the work of Bernardini and Ramacci[32] and Vrbaski[28], it may be concluded that the organic intermediates are readily oxidised to phthalic anhydride or to carbon oxides. The triangular scheme of Froment therefore appears to be an adequate representation of the oxidation over the 'German' catalyst. While rate data for the 'American' type of catalyst are lacking, it is of interest to note that the rate (per unit mass) of phthalic anhydride oxidation of Hughes and Adams, on an 'American' catalyst, is only one-tenth of that of Froment's scheme when projected to the same temperature range.

1.4 Catalyst Dilution

The most recent experimental study of o-xylene oxidation is that by Caldwell[30] who employed a fixed-bed reactor (1 inch i.d., up to 7 ft. of catalyst) to investigate whether the yield of phthalic anhydride might be improved by a policy of non-uniform catalyst dilution.

Earlier, Gilliatt[75] had shown experimentally that the yield of phthalonitrile (from the ammoxidation of naphthalene) could be raised by dilution, and Calderbank, Caldwell and Ross[76] demonstrated theoretically for a number of commercially important reactions that the use of dilution enabled the average temperature level in a tubular catalyst-packed reactor to be raised, and hence also the yield from a given reactor length. The technique should be applicable to all exothermic reactions where there is some constraint on the upper temperature but where a high yield is required from a single pass.

Using the triangular scheme and kinetics of Froment[12], Caldwell showed theoretically that by non-uniform dilution an improvement of up to ten percentage points in the yield could be obtained, and his experimental programme was undertaken in an attempt to confirm this.

Although Caldwell would have preferred a 'German' type catalyst since his predictions were based on one, he experienced difficulty in finding a manufacturer able and willing to supply him with a sample of commercial catalyst. He succeeded in obtaining a sample of promoted V_2O_5/SiC catalyst, which, apart from the promoter, is definitely of the 'American' type. This catalyst was used throughout his experimental work.

He found that no improvement resulted from dilution and that high temperatures appeared to be in no way detrimental to phthalic anhydride production. His results are discussed further in Chapter 5. It was clear from his results, however, that the behaviour of his catalyst was totally unlike that described by Froment's data.

1.5 Homogeneous Reaction

Several studies of the homogeneous oxidation of o-xylene have been reported in the literature.

Wright[54] detected 38 oxidation products - mainly carbon oxides, methane, hydrogen, water and toluene. Loftus and Satterfield[58] report o-xylene oxide as a major product and traces of phthalic anhydride among some fifteen other organic products of greater quantity.

Wright[59] and Burgoyne[60] both give an activation energy of 38 kcal/mole for the homogeneous disappearance of o-xylene; Denisova and Denisov[61] one of 31 kcal/mole; and Satterfield and Loftus[58] give a value of 20 kcal/mole. While the values of the rate constants given by these investigators vary widely, all show that the homogeneous rate is much slower than the catalytic rate.

An interesting exception is provided by the work of Satterfield and Loftus[62] who bubbled an air-xylene mixture through a melt of vanaduim pentoxide and potassium sulphate at temperatures between 528 - 598°C and found the catalytic rate data totally obscured by the homogeneous reaction.

Several of the catalytic oxidation investigators report oxidation catalysed by the reactor walls. Bernardini and Ramacci[32] report that in their empty stainless steel reactor 8 - 13% of the feed phthalic anhydride was oxidised at 500°C and a contact time of 0.14 secs., while in an empty glass reactor under the same conditions only 1% was oxidised. At half the contact time, the catalyst-packed reactors oxidised approximately 75% of the inlet phthalic anhydride. Similarly Hughes and Adams[21] found less phthalic anhydride combustion in a Pyrex reactor (2% at 575°C) than in an empty stainless steel reactor of the same design (~15%).

In contrast, Mann and Downie[39] and Juusola, Mann and Downie[41] found that o-xylene combustion was greater in an empty glass reactor than in steel, and the former found that even in steel the blank reaction was significant compared with the catalytic reaction at temperatures greater than 315°C.

However, both these groups employed a differential reactor and hence very low conversion levels.

1.6 Reaction Models and Mechanisms

Sensiman[63], in an early study of hydrocarbon oxidation on vanadium pentoxide catalysts, found that good yields of anthraquinone (from anthracene) could be obtained without the presence of oxygen in the gas phase, and that in the process the catalyst was reduced to the tetroxide. Weiss[64] reached similar conclusions from his study of benzene oxidation. Maxted[65] found that naphthalene, benzaldehyde and toluene oxidations all showed a good yield at about the same temperature on the one V_2O_5 catalyst, and from his observation that the rate of reaction was approximately the same for each of the hydrocarbons it was hypothesised that the reaction rate was mainly determined by the rate of reoxidation of the catalyst.

In 1954, Mars and van Krevelen[66] proposed the following mechanism for the oxidation of aromatics:

Reduced catalyst + oxygen $\longrightarrow$ oxidised catalyst

oxidised catalyst + hydrocarbon $\longrightarrow$ products + reduced catalyst.

They postulated that reaction took place between an organic molecule in the gas phase and oxygen from the catalyst lattice. The resulting oxygen deficiency in the lattice is made up by the uptake of oxygen from the gas phase. The rate of oxidation of the organic compound may be given by

$$R_N = k_N C_N \theta \qquad (1.1)$$

where θ is the degree of coverage of the catalyst surface by oxygen; and the rate of reoxidation of the surface by:

$$R_o = k_a C_o^n (1 - \theta) \tag{1.2}$$

If S moles of oxygen are required per mole of the organic, then at steady state

$$S\, R_N = R_o = S\, K_N C_N \theta = k_a C_o^n (1 - \theta) \tag{1.3}$$

Solving for θ gives

$$\theta = \frac{k_a\, C_o^n}{k_a C_o^n + S\, k_N C_N} \tag{1.4}$$

and therefore the rate of oxidation of the organic compound is

$$R_N = \frac{k_a C_o^n\, k_N C_N}{k_a C_o^n + S\, K_N C_N} \tag{1.5}$$

When a value of n = 1 is taken, the so-called Redox equation results:

$$R_N = \frac{k_a C_o\, k_N C_N}{k_a C_o + S\, K_N C_N} \tag{1.6}$$

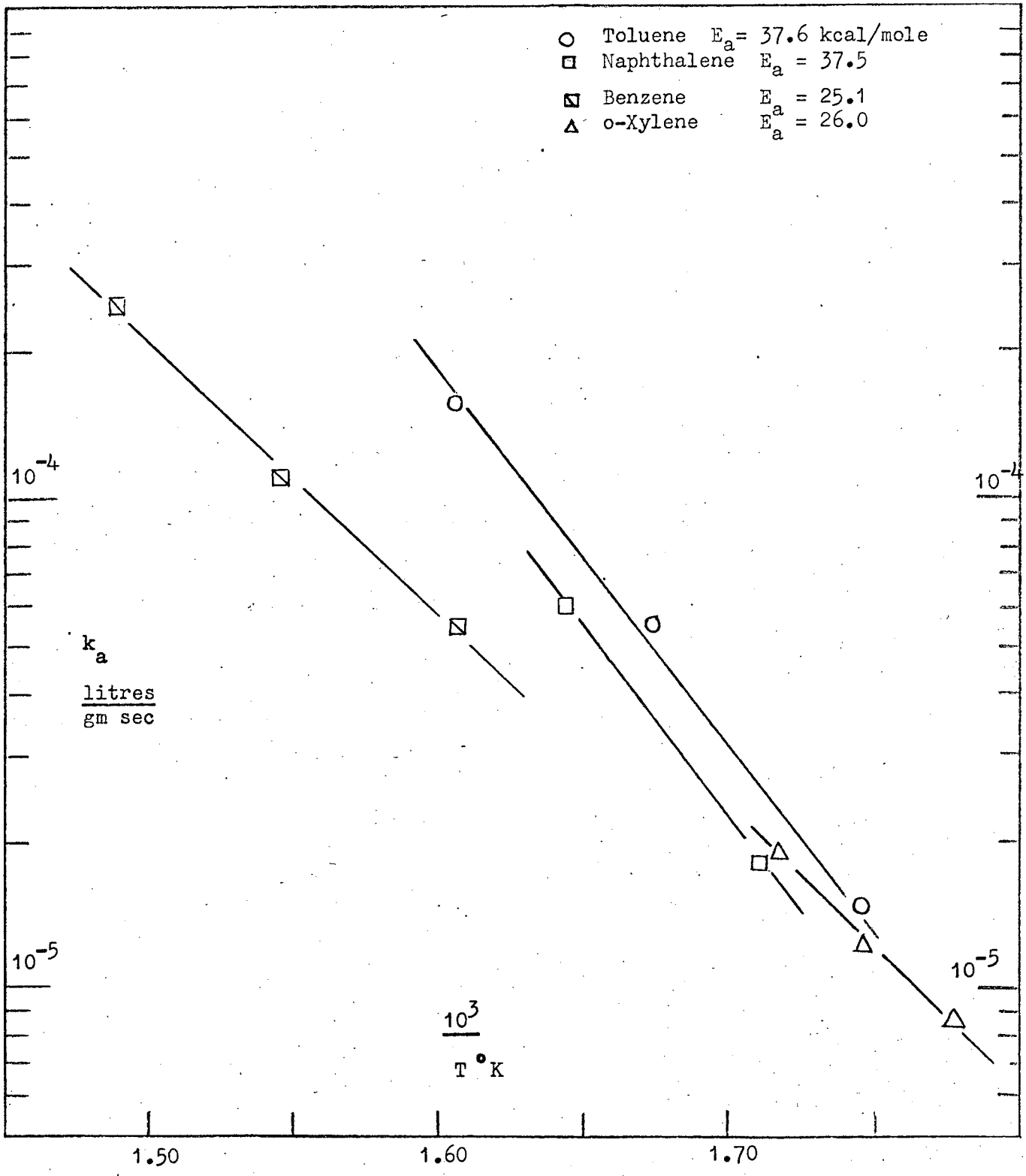
Mars and van Krevelen studied the oxidation of benzene, anthracene, naphthalene and toluene at conversions below 12% in a fluid-bed of $V_2O_5/K_2SO_4/SiO_2$ catalyst. Using an integrated form of equation (1.6) they obtained a reasonable correlation of their data; because of a concentration gradient of about 25% along the length of their reactor, they treated it as an integral one. As expected, Mars and van Krevelen found identical values for k_a for the oxidation of the different hydrocarbons over the same catalyst, with the exception of toluene. They report that they found a deviation for toluene, but give no information about it.

Since 1960 a series of papers has appeared describing studies of the oxidation of various aromatic compounds over the same catalyst[39,41,67-70]. In the first paper, Shelstad et al[67] proposed a model which is referred to as the steady state adsorption model (S.S.A.M.). In this model, reaction is postulated as occurring between gas phase hydrocarbon and surface-adsorbed oxygen, whereas Mars and van Krevelen assume that lattice oxygen plays a direct role in the reaction. The developed rate equation from the steady state adsorption model is identical to the Redox equation and so kinetic data cannot distinguish between them. The early workers[67 - 69] all correlated their data by linear technique, which involved inverting the rate equation, thereby weighting the errors non-uniformly. Jaswal et al[70] recalculated all their kinetic parameters by a non-linear technique and present the recalculated parameters of the previous workers with their own parameters for benzene oxidation. These values for k_a are presented in Figure 1.3 and the reasonable agreement among them may be considered as support for the model.

The early study of benzene oxidation on this same catalyst by Hayashi et al[69] reported a value for the activation energy of reoxidation of 8 kcal/mole and no carbon dioxide formation. This value is approximately $\frac{1}{4}$ of the mean value of the other studies. The later benzene oxidation study of Jaswal et al [70] used a more sensitive measurement system and found that carbon dioxide accounted for up to 90% of the reaction products. This highlights the precision required in differential reactor catalytic studies.

An unsatisfactory aspect of the studies of o-xylene oxidation by Mann and Downie[29] and by Juusola, Mann and Downie[41] is the difference between their hydrocarbon oxidation activation energies, the former reporting 9 kcal/mole while the latter reports 28 kcal/mole.

FIGURE 1.3


Toluene E_a= 37.6 kcal/mole
Naphthalene E_a = 37.5
Benzene E_a = 25.1
o-Xylene E_a = 26.0
10^{-4}
10^{-5}
k_a
litres
gm sec
$\frac{10^3}{T\ ^\circ K}$
1.50
1.60
1.70

While Mann and Downie do state that their value is approximate, it is obtained from a correlation of over 90 runs, and a temperature range of 25°C. Juusola et al plot the results of 82 runs in their paper, over a 20° temperature range, and so the studies are apparently of comparable magnitude; unfortunately, Juusola et al do not discuss this difference and mention the earlier study only indirectly.

Juusola et al[41] point out that where series reactions are occurring to a significant extent, the reactions of the intermediates should be included in the steady-state equation, since these reactions contribute to the disappearance of oxygen from the surface by chemical reaction. The rate equation then becomes:

$$R_N = \frac{k_a C_o \, k_N C_N}{k_a C_o + S\, K_N C_N + \Sigma S' K' C'} \qquad (1.7)$$

where the superscript $'$ indicates reoxidizable products. Juusola et al offer some criticisms of some of the supporting evidence for the Redox/S.S.A.M. equation. They criticise Mars and van Krevelen for assuming that the integrated form of the rate equation could be obtained directly from the differential form and used with high conversion data. Merten and Froment[38] successfully correlated their data with the Redox equation and Juusola et al suggest that their treatment, using the integrated form of the initial rate equation, is invalid because the oxidation involves a number of series reactions. They also criticise Vrbaski[56] for apparently using the differential form of the rate equation to interpret (high conversion) integral data. As Juusola et al themselves state, the integrated form can be obtained from the differential form and used with high conversion data only when series reactions do not occur to a significant extent.

Their criticisms seem therefore considerably over-stated. Mars and van Krevelen nowhere state their selectivities, their "high" conversions are less than 12% and they confine themselves mainly to determining the k_a parameter for the reoxidation of the catalyst. Vrbaski reports tolualdehyde as the major product in his study of methylbenzyl alcohol oxidation and it is very likely formed directly from the alcohol. While series reactions are occurring in Herten and Froment's work, the intermediate concentrations are relatively low and they use an experimentally determined value for S, thereby accounting for the total oxygen removal.

These successful correlations of experimental results also demonstrate the "data-fitting power" of the Redox/S.S.A.M. equation, which, by weighting of parameters, can vary from a zero order oxygen/first order hydrocarbon expression through to a first order oxygen/zero order hydrocarbon one.

Hughes and Adams[29] studied the oxidation of phthalic anhydride over a fused V_2O_5/SiC catalyst and found the rate of oxidation independent of the oxygen partial pressure above 0.1 atm., but varied with the phthalic anhydride partial pressure in a manner similar to a unimolecular surface reaction. They correlated their results by an expression of the form

$$\text{Rate of PA oxidation} = \frac{Ap}{1 + Bp} \qquad (1.8)$$

where p is the PA partial pressure, and A and B are temperature dependent parameters. They proposed the following mechanism:

$$\text{PA} + (\text{VO}) \underset{K_{-1}}{\overset{K_1}{\rightleftarrows}} (\text{VOPA})$$

$$(\text{VOPA}) \xrightarrow{K_2} (\text{V}) + (\text{O} - \text{PA})$$

$$(\text{V}) + O_2 \xrightarrow{\text{fast}} (\text{V})$$

i.e. a reversible adsorption, desorption of products and a rapid reoxidation of the catalyst. They showed that this mechanism led to equation (1.8) with

$$A = \frac{k_1 k_2 k'}{k_{-1} + k_2} \; ; \quad B = \frac{k_1}{k_{-1} + k_2} \; ; \quad A/B = k_2 k$$

(where k' is a conversion factor to convert from the fraction of surface covered to the true surface concentration). They considered two cases - (a) when $k_{-1} = 0$ and (b) when $k_{-1} \gg k_2$.

The first case is that of irreversible adsorption of reactant. The heats of activation for the irreversible adsorption of the reactant and for the desorption of oxidised product may be got from the temperature dependencies of A and A/B respectively.

The second case corresponds to an equilibrium adsorption with B equal to the adsorption equilibrium constant. The heat of adsorption in this case may be obtained from the temperature dependency of B. The heat of desorption is independent of the nature of the adsorption step. Values of A and B are reported for 497, 542 and 575°C, and the various activation energies are given. An exceedingly interesting experimental observation was that, below an oxygen partial pressure of 0.1atm., the rate of phthalic anhydride oxidation increased as the oxygen partial pressure decreased. The authors attribute this to a reduction of the catalyst. This point is discussed further in section 1.8.

If the oxygen partial pressure is assumed constant, then the Hughes-Adams equation (1.8) may be readily deduced from the Redox equation.

Callahan and Grasselli[71] suggest that the selectivity is largely determined by the number of occupied active oxygen sites which an adsorbed hydrocarbon molecule can contact. If there are only a few active oxygen sites, then a high selectivity to partially oxygenated compounds would be expected, whereas the greater the number then the greater the complete combustion. They do not postulate any surface mobility of either oxygen or hydrocarbon. They report some experimental results from their study of propylene oxidation which confirm their suggestion qualitatively.

Allen[72] discusses the mechanism of o-xylene oxidation with particular reference to the lattice and hydrocarbon molecule dimensions. It is estimated that the surface area of a $V_2O_5 - V_2O_{4.34}$ catalyst is approximately 12.2 $Å^2$ per available oxygen atom, while the area of an o-xylene molecule is approximately 33 $Å^2$. The oxidation of o-xylene to tolualdehyde (requiring two oxygen atoms per xylene molecule) would therefore be possible directly. As Allen rejects repeated adsorption/desorption of intermediates since they are rarely found in appreciable quantities in the reaction mixture, one is led to the conclusion that the formation of higher oxidation species requires mobility of one or both of the species.

1.7 Homogeneous-Heterogeneous Interaction

The investigators of hydrocarbon catalytic oxidations invariably conclude that homogeneous reaction should be minimised as it results mainly in complete combustion and is detrimental to the selectivities to the desired partially oxygenated products. In a recent lecture, however, Trimm[73] reported the results of an as yet unpublished study on benzene oxidation, which suggest a different conclusion.

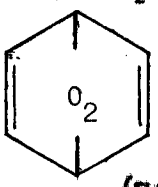
Trimm used a flow system and a small glass reactor which gave no homogeneous combustion of either benzene or maleic anhydride on a blank test. The early part of the reactor was then packed with catalyst and the free space between the end of the catalyst bed and the reactor exit varied by the addition of various materials. He reported that as the amount of surface was increased in this space (and therefore as the free space was decreased) a lower yield of maleic anhydride and a higher exit benzene concentration resulted. He was able to relate the yield of maleic anhydride to the volume of free space and found that the yield at minimum free space corresponded well with the catalyst bed voidage. He postulated the following scheme

$$\text{benzene} + \text{oxygen} \xrightarrow{\text{catalytic}} \text{intermediate} \begin{cases} \longrightarrow \text{benzene} \\ \searrow \text{maleic anhydride} \end{cases}$$

homogeneous

where a catalytically-formed intermediate reacts homogeneously to maleic anhydride and is capable of reverting to benzene on his surface material. From his yield/free space correlation he concluded that effectively all of the maleic anhydride is formed by this heterogeneous - homogeneous reaction path. It was suggested[40] to Trimm that the rise in the benzene concentration was suggestive of the existence of a homogeneous side reaction which consumed benzene and was suppressed by the addition of surface area. He believes[40] that this can be ruled out since a mixture of benzene and maleic anhydride failed to react homogeneously in his blank test and since, when the mixture was fed to a steel reactor, although the maleic anhydride underwent homogeneous reaction, the benzene did not, thereby confirming the non-interaction of one with the other.

The catalytic intermediate which he postulates is



similar to that postulated by Dmuchovsky[74] to result from singlet oxygen attack on the benzene ring.

It will be of considerable interest to see whether future workers can establish a similar heterogeneous - homogeneous path in other aromatic oxidations.

1.8 Nature of the Active Catalyst and Role of Lattice Oxygen

Since several of the investigations already discussed lead to the conclusion that vanadium pentoxide catalysts change their oxide state during catalysis and that the selectivity depends on the oxide state, it is of interest to consider the results of investigations into the nature of catalytically active vanadium oxides.

Simard et al[77] studied the structure of vanadium pentoxide catalysts after reaction with o-xylene. A catalyst which had been used for the oxidation of 1.1 mole% xylene in air was found to contain the crystalline phases V_2O_5, V_2O_4 and $V_2O_{4.34}$. The latter is a structurally well-defined oxide also known as V_6O_{13} and $V_{12}O_{27}$. Their electron diffraction measurements indicated that $V_2O_{4.34}$ overlaid V_2O_4 and therefore contacted the reactant gases. When the catalyst was used to oxidise a 3.3% xylene stream, which contained oxygen 100% excess of that required for phthalic anhydride formation, a hot spot progressed down the catalyst bed to the reactor exit, where a temperature more than 140°C above the bed control temperature was measured.

The catalyst in the bed was completely inactive but could be restored by prolonged heating in air. V_2O_4 and some V_2O_3 at the reactor exit were the only oxides found and were thus concluded to be catalytically inactive. The authors conclude that V_2O_5 and $V_2O_{4.34}$ are the catalytically active species.

Simard et al[77] also found that a 1.1% xylene in oxygen-free nitrogen stream could be oxidised to phthalic anhydride with an accompanying reduction of the catalyst to a mixture of V_2O_5, $V_2O_{4.34}$ and a trace of V_2O_4. They conclude from this result that the hydrocarbon reacts with lattice oxygen during catalytic oxidation.

Volfson et al[80] compared the activity of the same oxides in the catalytic oxidation of naphthalene and came to the conclusion that the catalytically active species was V_2O_4, formed from V_2O_5 via $V_2O_{4.34}$, both of which were relatively inactive. Schaefer[81] reached a similar conclusion in his study of benzene oxidation - V_2O_4 had the highest activity, while $V_2O_{4.34}$ had slight activity and V_2O_5 and V_2O_3 were inactive. Farkas[82], in a recent review article, attributes this apparent discrepancy in the active oxide to the difference in the nature of the aromatics studied.

Clark and Berets[83] investigated the electrical properties of vanadium pentoxide catalyts and report that lattice defects are quite mobile in the surface region below 180°C, but are mobile in the bulk only above 350°C.

Ushakova et al[78] observed that the selectivity of vanadia oxides in oxidising naphthalene to phthalic anhydride was dependent upon the ratio of V_2O_4 to V_2O_5 in the catalyst. While a 79% V_2O_4 and 21% V_2O_5 catalyst was highly active for oxidising naphthalene, the yield of phthalic anhydride was poor because the catalyst promoted considerable phthalic anhydride combustion.

In contrast to the suggestion of Callahan and Grasselli[71] that complete combustion is greater on a fully oxidised catalyst, Vrbaski[56], Hughes and Adams[29], Vrbaski et al[42] and Butt et al[79] all, like Ushakova, believe that a reduced catalyst promotes abundant formation of carbon oxides.

While Simard et al[77] concluded that the hydrocarbon reacts with lattice oxygen during catalytic oxidation, they merely showed that in the absence of gas-phase oxygen, the hydrocarbon could react with lattice oxygen. They give no rate data to indicate whether it proceeds at a rate significant in magnitude to the normal cotalytic rate in the presence of oxygen. Recent work has cast some doubt on the validity of the alternate reduction-oxidation mechanism.

Odrin et al[84] have reported that the rate of the catalytic oxidation of naphthalene on vanadia is an order of magnitude greater than the reduction or oxidation of the catalyst. Schaefer[81] reports kinetic parameters for benzene oxidation over V_2O_4, V_2O_5 and three intermediates oxides, in both the presence and absence of gas-phase oxygen. With the exception of $V_2O_{4.66}$, the latter rates are approximately $\frac{1}{4}$ to $\frac{1}{10}$ of the rates in the presence of oxygen. The reduction in the case of $V_2O_{4.66}$ is nearer one-half.

Roiter[85] observed no O^{18} in the oxidation products when naphthalene was oxidised in the presence of an O^{18} enriched vanadia catalyst. In a later review, Boreskov[86] expresses some doubt about Roiter's conclusion that lattice oxygen does not participate in the reaction, because of the low mobility of oxygen inside vanadia at the temperature of his study.

However, Roiter in a different study[88], used O^{18} exchange to determine the activation energy for oxygen exchange between gaseous O_2 and V_2O_5 (37 kcal/mole) and found that the rate of exchange was not increased if SO_2 was being oxidised. Many workers, including Mars and van Krevelen[66], have proposed a 'Redox' scheme for SO_2 oxidation on vanadia. Roiter[89] has also reported that the oxidation of CO on MnO_2 and on CuO catalysts proceed without O^{18} exchange. Margolis et al[87] reached a similar conclusion.

It may therefore be concluded that while there is still disagreement about the activity of the various vanaduim oxides and about the participation of lattice oxygen in the reaction, the weight of evidence is gathering against direct participation of lattice oxygen.

1.9 Object of this Study

This study was originally intended to be an investigation of the fluidised-bed oxidation of o-xylene, in view of the number of unsolved problems relating to this process (discussed in section 1.2.3).

Shortly after the commencement of this study, however, Caldwell[30] obtained results from his study of the fixed-bed oxidation of o-xylene, with and without catalyst dilution, which showed that his 'American' type catalyst was behaving in a manner quite unlike that described by Froment's[12] 'German' type kinetic data.

Since there was a general lack of data for 'American' type catalysts, it was then decided to investigate the kinetics of o-xylene oxidation over Caldwell's 'American' catalyst, to thus elucidate some of his results and to provide the kinetic basis from which a fixed-bed reactor mathematical model might be developed.

Therefore only a preliminary investigation of the fluid-bed oxidation was conducted.

Chapter 2

Experimental Equipment and Procedure

The reactor used for the study of the kinetics of o - xylene oxidation was a stirred catalytic reactor, chosen for its many advantages over other types of experimental reactors, viz:-

a) the good mixing of the system eliminates mass and temperature gradients in the bulk phase.

b) the good mixing also eliminates mass transfer limitations at the catalyst surface, and minimises temperature differences between the catalyst and bulk fluid.

c) at steady-state conditions, the analysis of the product stream from the reactor yields the exact concentrations occurring in the reactor. Reaction rates are obtained by a simple mass balance, input minus output divided by time.

d) the kinetic data may be obtained without the use of procedures such as integral analysis or limiting conversion to allow a differential analysis to be performed, with their inherent large errors.

e) unlike a fluidised bed, there are no physical problems such as catalyst attrition or carry-over of fines, which could give reaction outside the reactor.

Set against these are two disadvantages which were not considered to be sufficiently serious to cause the choice of the type of reactor to be changed:-

a) when the reaction is at steady-state, the inlet conditions immediately change to the reactor concentrations which may be very different from those at the inlet.

Unless a very rapid analysis is available, it is not practicable to employ the normal kinetic procedure of varying one reactant concentration while the others are held constant. The data must be considered as a whole.

b) because of this the ability to plan subsequent experiments is reduced, since an analysis of the results requires a considerable amount of data.

Several different models of stirred catalytic reactors have been described in the literature in the past few years, notably by Carberry et al [43], Garanin et al [44] and Brisk et al [45]. The use of a spinning catalyst-basket reactor of the type developed by the latter was obtained from I.C.I. Central Instruments Research Laboratory, who extended the loan of the reactor used by Ross[31] (for his study of naphthalene oxidation), for this study. This reactor is frequently abbreviated to C.S.T.R. in subsequent discussion.

In addition, a fluidised-bed catalytic reactor was constructed to enable a brief study to be made of the fluid-bed xylene oxidation. It was found advantageous, for the purpose of comparison of results, to operate this fluid-bed reactor as a fixed-bed, at conditions intermediate to those in the C.S.T.R. and Caldwell's reactor.

The reactors and their associated equipment are described in the following sections.

2.1 The Spinning Catalyst-Basket Reactor Apparatus (The C.S.T.R.)

This equipment is shown schematically in Figure 2.1

The gases used - air, oxygen, nitrogen - were supplied from high-pressure gas cylinders, regulators being used to reduce their pressures to approximately 4 p.s.i.g.

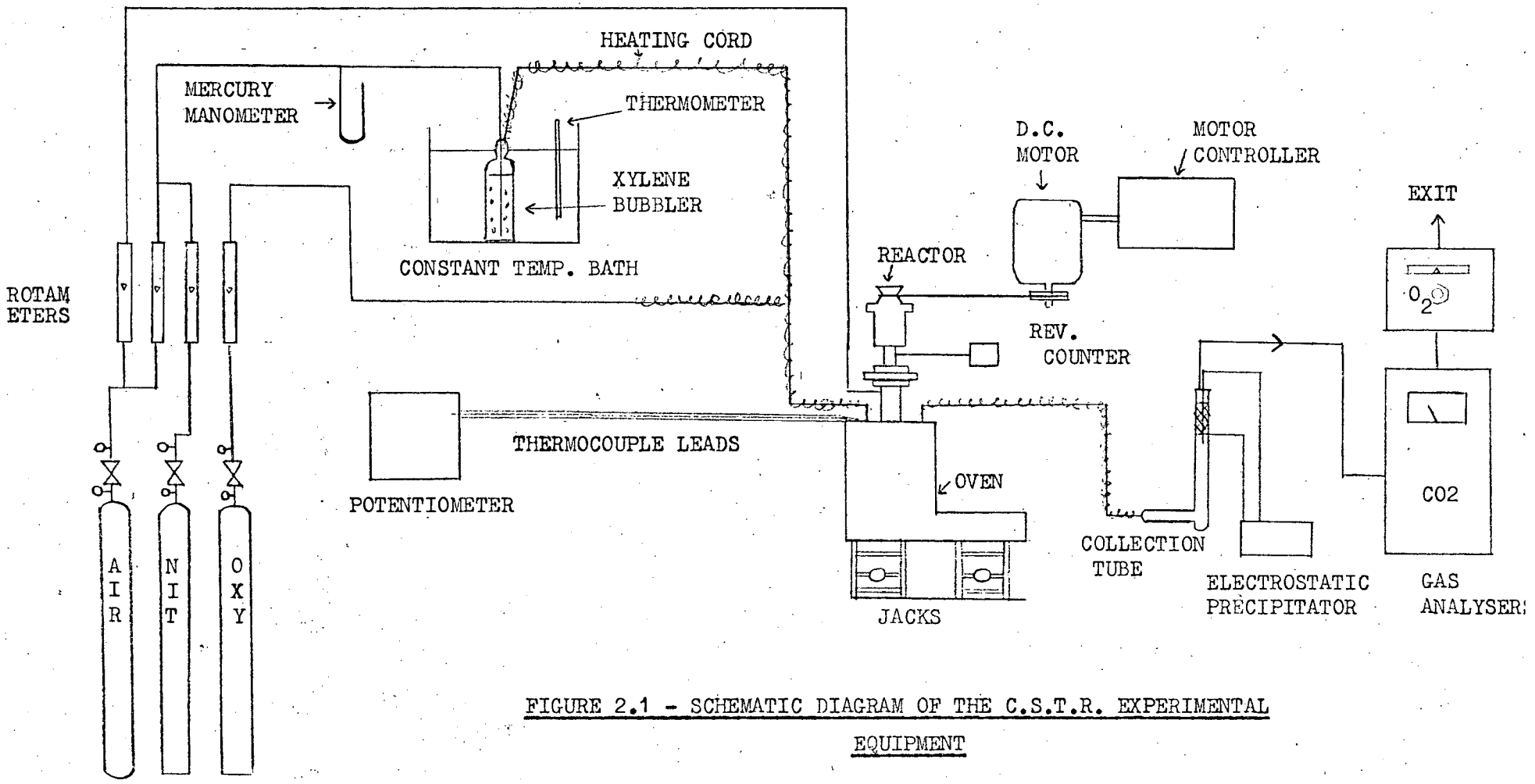


FIGURE 2.1 - SCHEMATIC DIAGRAM OF THE C.S.T.R. EXPERIMENTAL EQUIPMENT

Four rotameters were employed to meter the reactor inlet gas stream, which consisted of three parts:

a) the xylene input stream

b) the bubbler bypass stream

c) the shaft purge stream

Two of the rotameters connected in parallel measured the flowrate of the xylene input stream. The air cylinder was connected to the larger of the two, and the nitrogen cylinder to the smaller, thus permitting variability of the oxygen inlet concentration. These two streams were mixed after passing through the rotameters and the line pressure was measured with a mercury manometer. This pressure never exceeded 2 cms. Hg. gauge. The combined flow then passed through a bubbler containing (liquid) o - xylene at constant temperature. The stream from the bubbler, containing xylene, entered the reactor through a port in the top of the vessel. The lines from the bubbler to the reactor were heated with Thermotrace heating cord and insulated with asbestos tape to prevent xylene condensation.

Normally the hydrocarbon-rich feed to the reactor would be split and introduced through two ports on opposite sides of the reactor shaft, thereby improving the mixing. However, since xylene has a considerable vapour pressure at room temperature ($\sim$ 7 mm), small inlet concentrations of xylene would not be achieved if the total input stream passed through the bubbler, unless the bubbler was cooled below room temperature.

Instead, another inlet stream was introduced - the bubbler bypass stream. After passing through a rotameter, this stream (air or oxygen or nitrogen) was fed directly to the reactor through the second port on the top of the vessel.

The third inlet stream - the shaft purge stream - was introduced down the drive shaft of the reactor to prevent possible product condensation on the shaft bearings. This stream never exceeded 10% of the total flow, and was usually considerably less.

The rotameters, supplied by the Rotameter Manufacturing Co., had stainless steel needle valves and couplings, and had the following ranges for air at 15°C and 1 atmosphere:

Xylene input	:	220 ml/min
		90 ml/min
Bubbler bypass	:	150 ml/min
Shaft purge	:	80 ml/min

The reactor was a stirred catalytic reactor, the catalyst being contained in a rotating basket, which was driven by a variable-speed D.C. motor through a magnetic coupling. The speed of rotation was indicated by a tachometer connected to a reed relay. The reactor temperature was measured with three nickel-chromel/nickel-alumel thermocouples connected through a selection switch to a potentiometer and a millivolt recorder. A Perkin-Elmer precision oven was used to heat the reactor and to control the temperature.

The reaction products left the reactor through an outlet pipe located in the bottom of the vessel and were fed to a glass collection tube where the organic products (but not all of the exit xylene) were precipitated with a 6000 volt electrostatic precipitator.

The exit gases from the collection tube were periodically fed to gas analysers to ascertain the concentrations of oxygen and carbon dioxide. For the remainder of the time, the gases were exhausted through a water ejection pump.

The lines from the reactor to the collection tube were also heated and insulated to prevent product condensation.

All tubing, except the two 1/8th inch o.d. stainless steel reactor inlet lines, was 1/4 inch o.d. stainless steel. British Ermeto stainless steel fittings were used for the necessary connections.

2.1.1 Xylene Addition

o - Xylene was added to the reactant mixture by bubbling part of the inlet gas stream through liquid xylene. The bubbler, a 250 ml. Quickfit Drechael Bottle with porosity '0' sintered head, was immersed in a water constant temperature bath which gave temperature control within $\pm$ 0.1 ^{o}C. A small hole was made in one bubbler glass top and a thermocouple placed through it and sealed with Araldite, thus permitting measurement of the vapour exit temperature. This always corresponded to the bath temperature, and so, when this bubbler top was broken, no thermocouple was placed in successive tops.

The gap between the surface of the water bath and the heating cord, which was wrapped around the outlet of the bubbler, was kept as small as possible.

Satisfactory connection of the stainless steel tubing to the glass bubbler was achieved by the use of Quickfit Double Screwtop joints. These consisted of a tubular glass section, threaded at both ends, with an inside diameter sufficient to allow the tubing to fit loosely inside. A threaded plastic cap compressed a silicone rubber ring and a thin teflon guide ring around the tubing and against the glass section at each end giving a gas-tight seal.

As the plastic caps were unable to withstand the direct heat application of the heating cord, brass threaded caps were made. As the brass expanded more than the glass, a slight tightening of the cap at temperature was necessary to obtain a leakproof seal.

These joints were easily opened and reformed to permit xylene to be added to the bubbler, and were of sufficient flexibility to prevent damage from the vibrations from the reactor drive and bath stirrer.

2.1.2 The Spinning Catalyst-Basket Reactor

The reactor, shown in Figure 2.2, was a stirred catalytic reactor on loan from I.C.I. Central Instruments Research Laboratory.

The reactor consists of a cruciform basket, containing catalyst, rotating in a 60 cm^3 reactor pot. The basket was bolted to the bottom of a shaft, 12 inches long, which was completely enclosed and ran on enclosed rulon bearings. The shaft was driven by rotating an outer casing which contained permanent magnets locked on magnets located in the top section of the shaft. The lower section of the inner magnet provided a signal for a tachometer through a reed relay. A small flow of air - the shaft purge stream - was introduced through a pipe in the shaft casing to prevent diffusion of the organic compounds up the shaft where they might solidify on the bearings. The outer magnet casing was driven by a 1/4 h.p. D.C. motor through a v - belt. The power supply to the motor came from a rectifier-speed control unit. A maximum basket speed of 4000 r.p.m. was obtainable.

The top plate of the reactor pot (Figure 2.3a) contained two inlet ports, three thermocouple ports and a pressure tapping. The inlet ports were positioned on opposite sides of the shaft and fed directly onto the outside edges of the catalyst basket.

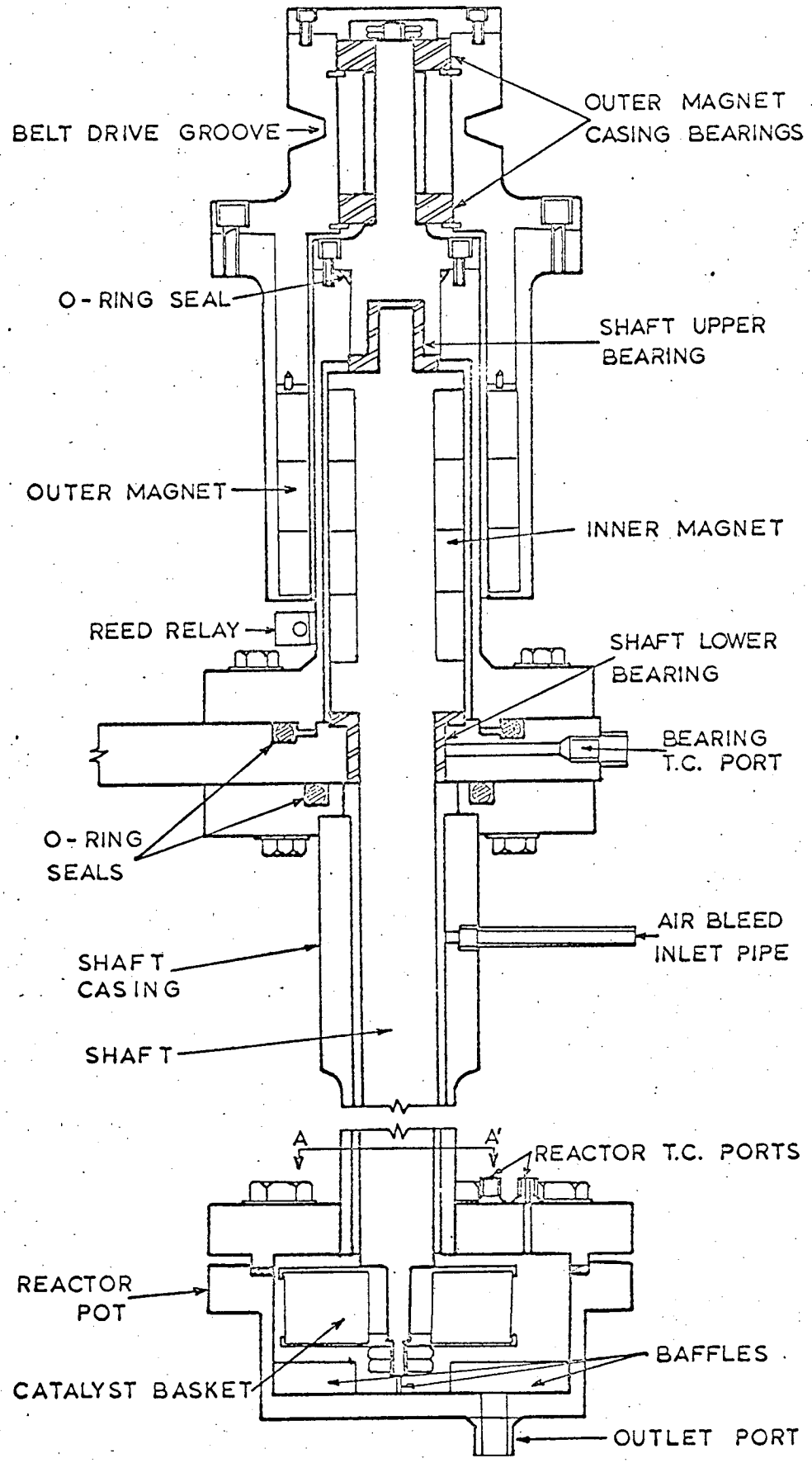
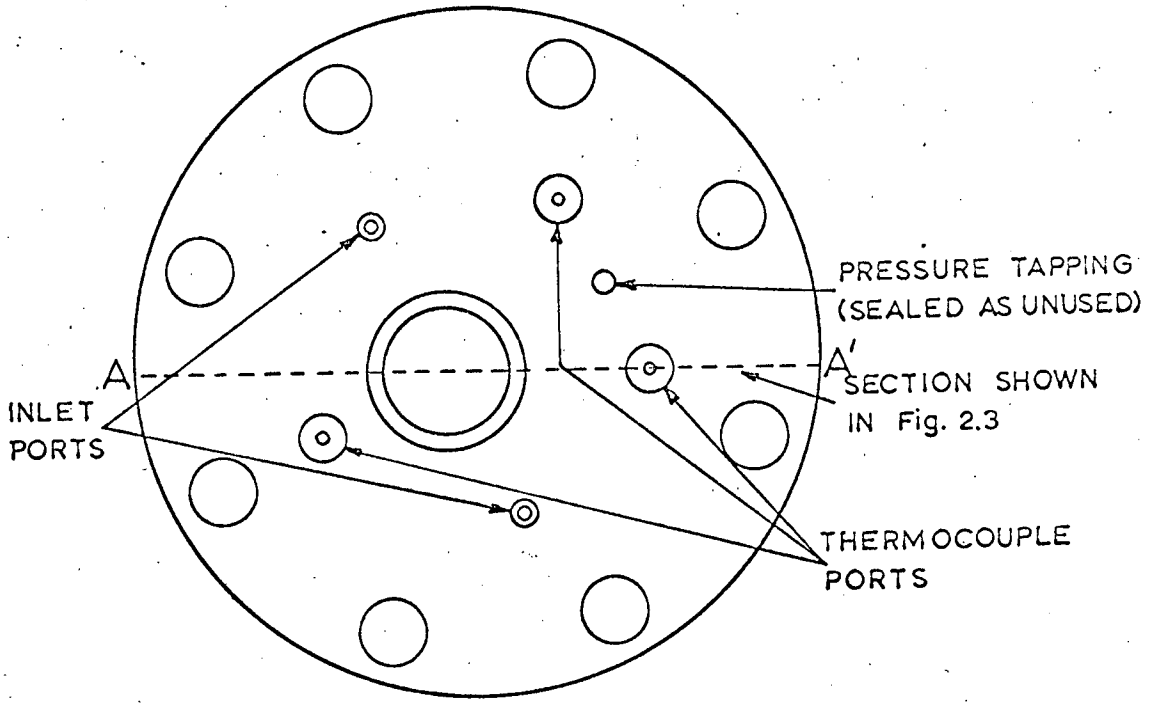


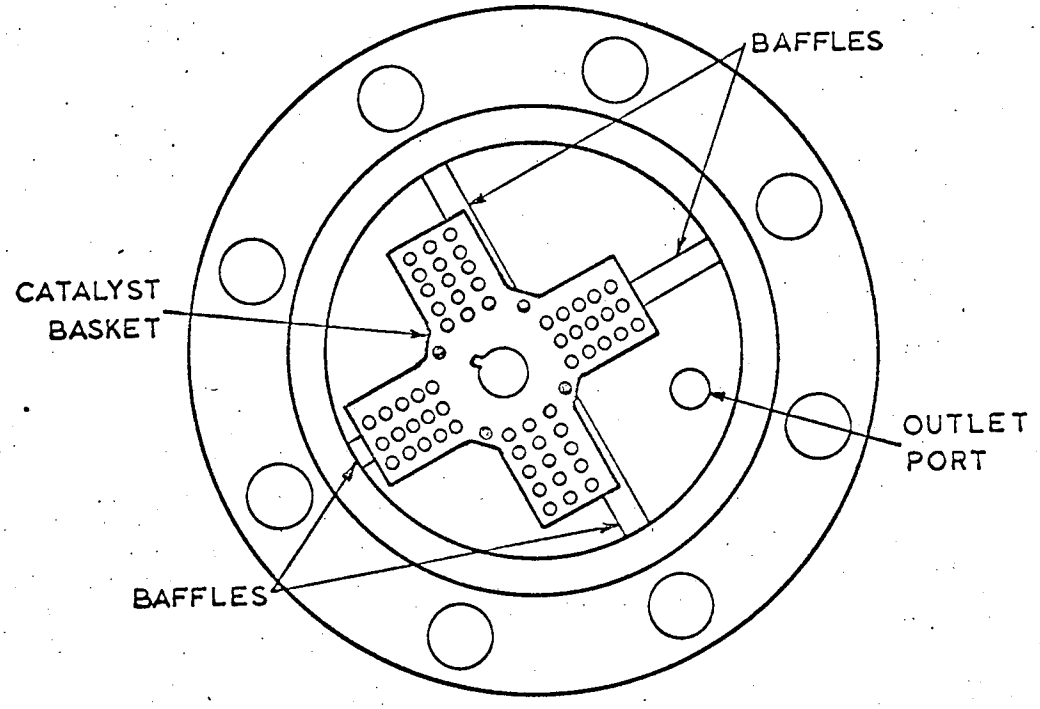
FIGURE 2.2 - THE SPINNING CATALYST BASKET REACTOR

SCALE ARBITRARY

FIGURE 2.3



(a) SECTION ON A-A' Fig. (shaft and reactor pot removed, scale-full size)



(b) REACTOR POT AND CATALYST BASKET

As already stated, the xylene-containing stream was introduced through one of these ports, the bubbler bypass stream entering through the other. The shaft was not concentric with the reactor pot. The location of the thermocouple ports allowed the temperature to be measured directly over the catalyst basket, in the middle of the unswept volume of the reactor and at the bottom of the reactor near the outlet port. Because the products would solidify in the lines, no pressure measurements were taken and the pressure tapping was sealed. The reactor pressure would be essentially atmospheric, in any case, as the exit line was open to atmosphere.

The reactor pot (Figure 2.3b) had four baffles on the bottom running radially from the centre of rotation of the basket to the walls. An outlet pipe was located in the bottom of the pot in the area unswept by the basket. The catalyst basket, with an approximate capacity of 4 cm^3 had perforated plates top and bottom and wire mesh sides. An asbestos gasket was used to seal the reactor pot to the top plate.

All parts of the reactor in contact with the reaction mixtures were of stainless steel, with the exception of the basket mesh which was nickel.

The flow of gas in the reactor is extremely complicated and the degree of mixing cannot be calculated. Pulse response and reaction work by I.C.I. have determined the speeds required for perfect mixing at various inlet flowrates [45, 46]. At 3000 r.p.m., which was used throughout this work, flowrates of up to 0.8 litres / min will still give a well mixed reactor. Poor mixing does not occur until flow rates in excess of 1.1 litres/min. are reached. The flowrates used in this kinetics study rarely exceeded 0.4 litres/min. and only once exceeded 0.5 litres/min.

A Perkin-Elmer Precision Oven was used to heat the reactor and gave temperature control within $\pm$ 1°C. A 1½ inch thick asbestos block, cut to fit the shaft casing and inlet and outlet lines, was used as a lid for the oven. A maximum temperature of 485°C (oven maximum = 500°C) could be achieved. The oven was supported on screw jacks which enabled it to be lowered easily for catalyst changing.

2.1.3 Product Collection

The products were condensed out of the exit gas stream by passing the flow through a ½ inch i.d. 'L' - shaped glass tube which was at room temperature. A small bulb at the heel of the L retained any liquid condensed. An electrostatic precipitator was used to precipitate any solid particles small enough to be carried out of the collector by the exhaust gases. In practice, not all of the exit (unreacted) xylene was collected. Attempts to improve the xylene collection are discussed in section 2.5.1.

Approximately 5800 volts were applied across the electrodes of the precipitator from a 240 - 6000 volts transformer, the input voltage of which was controlled by a variac. The outer electrode was copper gauze wrapped around the top third of the collection tube. The inner electrode was a thin steel rod held in place by a rubber stopper through which it was pushed. A piece of glass tubing inserted through the rubber stopper directed the exhaust gases to a suction line. This line, with a water ejection pump providing the vacuum, was placed near, but not coupled to, the exit to prevent accumulation of organic vapours in the laboratory atmosphere.

Periodically during a run, a nylon tube, leading to the gas analysis equipment, was coupled directly to the exit glass tube to permit the measurement of the exit oxygen and carbon dioxide analysis.

The coupling of the glass collection tube to the steel tubing from the reactor was achieved in the following way. A Quickfit ground glass ball joint was fixed to the toe of the 'L' - shaped tube. This ball joint fitted into a machined stainless steel cone, the back portion of which was reduced to 1/4 inch, enabling connection to be made to the stainless steel tubing through a standard British Ermets coupling. The glass collection tube was held in place by spring clips. The sealing pressure came from the flexibility in the tubing coming from the reactor.

This joint was leakproof at up to 10 p.s.i.g., and could be made and broken very quickly for accurate timing of the collection runs.

2.1.4 Analysis Equipment

The organic products collected, o - xylene, o - tolualdehyde, maleic anhydride, o - toluic acid, phthalide and phthalic anhydride, were analysed using a Perkin-Elmer F11 Dual Column Gas Chromatograph. As already stated, not all of the exit xylene was collected. A schematic diagram of the basic lay-out of the chromatograph is shown in Figure 2.4. The chromatograph was fitted with a hydrogen flame ionization detector, and a linear temperature programmer was used to improve the separation of the compounds. An electromechanical integrator was used to determine peak areas.

The supply gases - air, hydrogen and (oxygen free) nitrogen - were controlled by standard pressure reducing valves on the supply cylinders and then by a precision pressure control unit. The air and hydrogen pressures used were 29 and 12 p.s.i.g. respectively as these gave a high signal output combined with good stability for the analyses carried out. The two nitrogen flows were at pressures of approximately 25 p.s.i.g., fine adjustment being made on the pressure control unit to give a balanced signal at the maximum operating temperature.

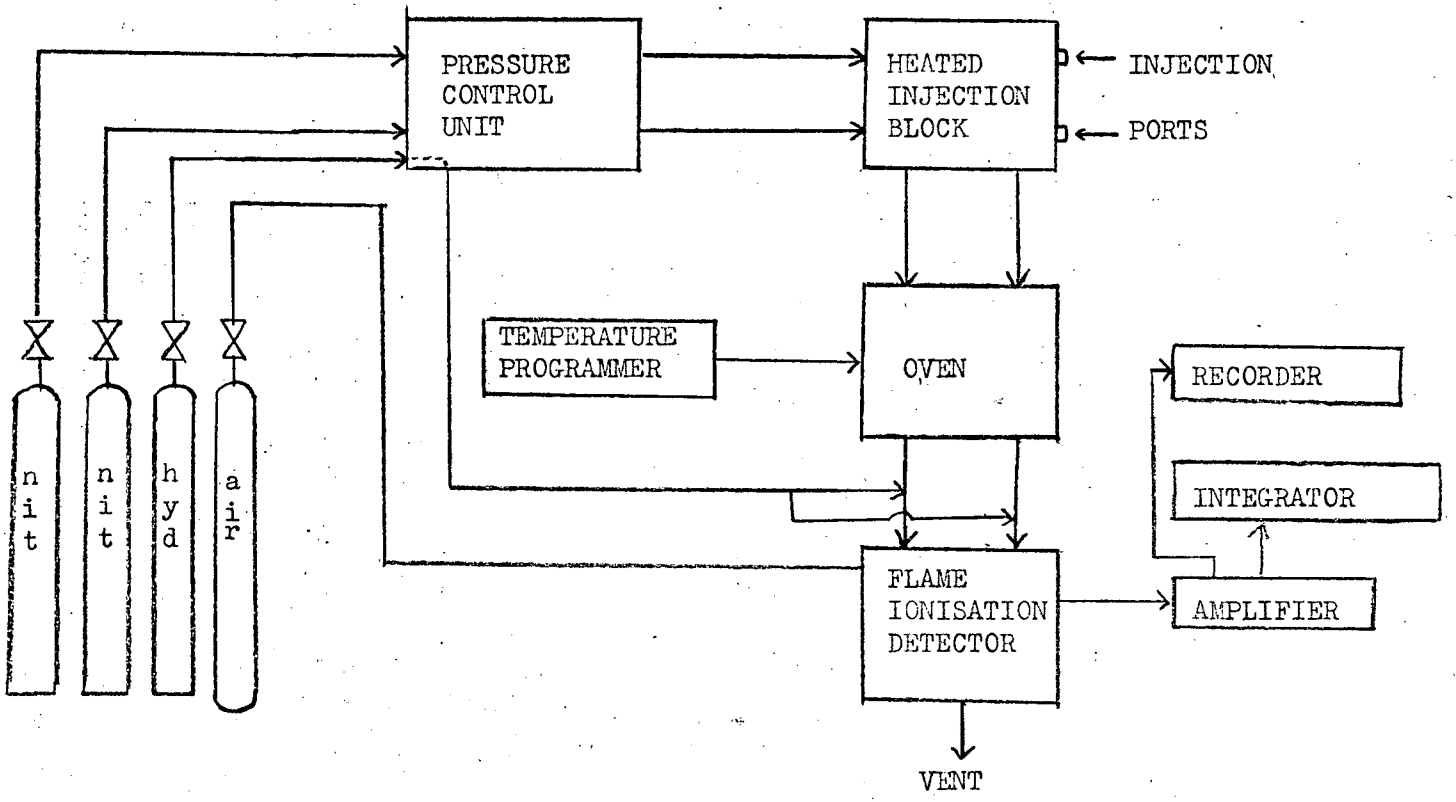


FIGURE 2.4 - SCHEMATIC ASSEMBLY of F11 CHROMATOGRAPH

Baseline drift due to column bleeding was effectively eliminated during the temperature program.

Each nitrogen flow passed through an injection block, heated to approximately 300°C, and into the column. Samples were injected with a one microlitre syringe, through a high-temperature rubber septum into one column exclusively. The exit gases from the columns were ionized in the hydrogen flame and the ionization current from the detector was amplified and fed to an integrator and recorder. The recorder, a Leeds Northrup, Type W, Model S, was used to check for tailing and baseline drift. The integrator was a Kent Chromalog MK1, consisting of a pre-amplifier, a current - to - frequency converter and a print-out counter.

This integrator was out of use for some days due to a printer fault. During this time, analyses (for approximately 20 runs) were done using a Kent Chromalog MK3.

The tail gas analysis equipment consisted of a Grubb Parsons Infra-red Gas Analyser calibrated for carbon dioxide, and a direct reading Servomex OA101 MK2 oxygen analyser.

2.1.5 Catalysts used in the Spinning Catalyst-Basket Reactor

The catalysts used for the study of oxidation of o - xylene was that used by Caldwell[30] in his study of fixed-bed xylene oxidation.

In addition, a few runs were made for comparison purposes using other vanadium oxide catalysts. The catalysts are listed below.

Catalyst 1 (The same as Caldwell's)

This was a surface coated V_2O_5 catalyst, with undisclosed promoters, on silicon carbide. It is not known if this catalyst is, has been or will be employed industrially, but it was supplied by a firm making industrial catalysts.

Size range: 0.3 - 0.8 cms. (Particles of approximately 0.5 cms. were used in this reactor).

True density (He)	: 2.84 gm/cm^3
Particle density (Hg)	: 2.55 gm/cm^3
Pore volume	: 0.04 cm^3/gm
Pore radius	: 4444 A
Surface area	: 0.2 m^2/gm (approx.)

As the use of a stirred catalytic reactor eliminated the bulk phase temperature and concentration gradients, a low porosity catalyst was preferred to limit the possibility of pore diffusion and thus allow determination of the reaction kinetics unaffected by transport processes. This catalyst is patently satisfactory in this respect.

Catalyst 2

This catalyst was the one principally used by Ross[31] for the oxidation of naphthalene.

3.5% V_2O_5, 1.5% S_nO_2 on 95% (nominal) fused alumina.

Size range :	0.132 - 0.110 inches
Surface area :	< 1 m^2/gm
Apparent porosity of support	~ 5%
Chemical analysis of support	~ 99% alumina

Catalyst 3

V_2O_5 and K_2SO_4 on silica.

Size : 3/16 x 3/16 inch cylindrical pellets

No further information was available.

2.1.6 Chemicals

Phthalic anhydride (99% purity), o - toluic acid (99%), and maleic anhydride (99.5%) were supplied by British Drug Houses Ltd. Phthalide (> 95%) was obtained from Hopkin and Williams Ltd., and o - tolualdehyde (95 - 99%) from K and K Laboratories Inc., via their U.K. distributors, Kodak Ltd.

The o - xylene was supplied by R.N. Emanuel Ltd., Wembley, and was of >99% purity. Caldwell obtained his xylene from this same supplier.

Naphthalene of 'Organic Analytical Standard' grade from B.D.H. Ltd., was used as an internal standard in the chromatographic analyses.

All of the compounds gave good single peaks (o - xylene had a negligibly small peak superimposed on the tail) except for the tolualdehyde. In addition to one large peak, it gave four small peaks, the sum of whose areas, however, was less than 10% of the large peak area.

High purity 'Analar' grade acetone was supplied by B.D.H. Ltd.

The air, nitrogen, oxygen and hydrogen were obtained from the British Oxygen Company Ltd., and were of 99.7% minimum purity. The carbon dioxide used to check the calibration of the CO_2 meter was supplied by the Distillers Co. Ltd., and had a minimum purity of 99.8%.

2.1.7 Experimental Procedure

a) Kinetic Runs

As some difficulty was experienced in obtaining significant reaction rates at the lowest reaction temperature used in this study on occasions where the catalyst had been newly heated from room temperature, the oven was normally kept at 400°C when runs were not being performed. The constant temperature bath was allowed to run continuously as it required several hours to become stable at the set temperature.

Before a run began, the oven was set to the desired temperature, the reactor bearings cooling fan was switched on, as were the line heating cords. After approximately five minutes, the reactor drive motor was switched on and the basket rotational speed set to an indicated 3100 r.p.m. (an actual 3000 r.p.m.). The gas flows were turned on an adjusted to the required rates. Flow rates and temperatures were checked, and, if necessary, adjusted regularly during a run.

After approximately one hour a tail gas analysis was made to determine the oxygen and carbon dioxide concentrations. The first product sampling was begun after approximately a further thirty minutes. An 'L' - shaped tube, with precipitator leads attached, was connected at the start of the collection period, and the precipitator quickly switched on. The duration of a collection period was normally thirty minutes, but never more than thirty-three. The precipitator was turned off five seconds before the end of the collection and the tube removed. The precipitator leads were disconnected and the tube was waved in the air to cool the end that had been coupled to the hot steel cone and so prevent the products from vapourising and diffusing out of the tube.

A second gas analysis was made after a further 15 minutes and a second product collection began 15 minutes after that. Finally a third tail gas analysis was taken soon after the completion of the second product collection.

The shutdown procedure was to turn off the xylene input stream and to turn up the bubbler bypass stream to its maximum to clear the reactor of any organic products. After approximately 2 - 3 minutes, all gas flows, the heating cords and the reactor drive and cooling fan were turned off. The oven temperature was set to 400^{o}C, and, if desired, the constant temperature bath was altered before the next run.

b) Product Analysis

The condensed products in the collection tube were washed into a sample bottle with three successive volumes of acetone, in total approximately 30 ml. An exactly known weight of naphthalene (approximately 0.1 g) was added.

Using a microlitre syringe, a 1.0 microlitre of the sample was injected into the chromatograph which was operated on a temperature programme which held the oven at 40°C for 3 minutes and then raised it by 12°/min to a final temperature of 140°C. The peak areas printed out by the integrator were sealed to a standard naphthalene area and the amount of each component found from the calibration graphs. Details of calibration are given in section 2.6.6.

The results of the analyses of the two samples were compared. If the amounts of phthalic anbydride were within 3% and all other components within 10%, agreement was considered good and no further analyses were done. It should be noted that phthalic anhydride was normally present in considerably greater quantity than the other products. If the agreement was poorer than this, both samples were analysed again. If agreement was still poor, then the run was noted as suspect, possibly not at steady state conditions.

Two rigs were frequently being operated at the same time, samples being taken from both of them. Because of this and because of the time required to analyse a sample, it was not always possible to analyse samples as soon as they were taken, or sometimes on even the same day that they were taken. Therefore samples were stored in a refrigerator until they could be analysed. No difference was apparent in a sample which was left for a week, nor in a synthetic solution of the products which had been left for six weeks.

The Fixed-Bed/Fluidised-Bed Reactor Apparatus

This reactor was designed as a fluid-bed reactor, but was in fact first operated as a fixed bed. Only minor changes were necessary to change from one mode of operation to the other.

2.2 The Fixed-Bed Reactor Apparatus

This equipment is shown schematically in Figure 2.5.

Air from a small compressor (an Edwards R.B.5) was passed through a cotton-wool filter to remove any entrained oil, through a silica gel drying column and through a combined Aerox filter and pressure regulator unit to the two metering rotameters. At a later date, the Edwards R.B.5. was replaced with an Edwards 'Reciprotor' pump which had teflon reciprocating pistons which did not require lubrication.

The larger rotameter (0 - 10 litres/min of air at N.T.P.) was used to measure the bypass stream which was fed directly to the reactor, the smaller (0 - 700 ml/min) to measure the xylene input stream which passed through a xylene bubbler in a constant temperature bath. The two streams were mixed prior to entering the reactor.

The reactor consisted of an aluminium cylindrical block, twelve inches in length by six inches in diameter, with a two inch hole drilled along its major axis. The catalyst was supported on a stainless steel sintered plate held in position by the bottom flange piece. The reactor was heated via 150 ft. of resistance wire round the block.

The products were collected in an air condenser which had at its exit a cylindrical can filled with glass wool.

All tubing was 3/8 inch o.d. stainless steel, the couplings being British Ermeto.

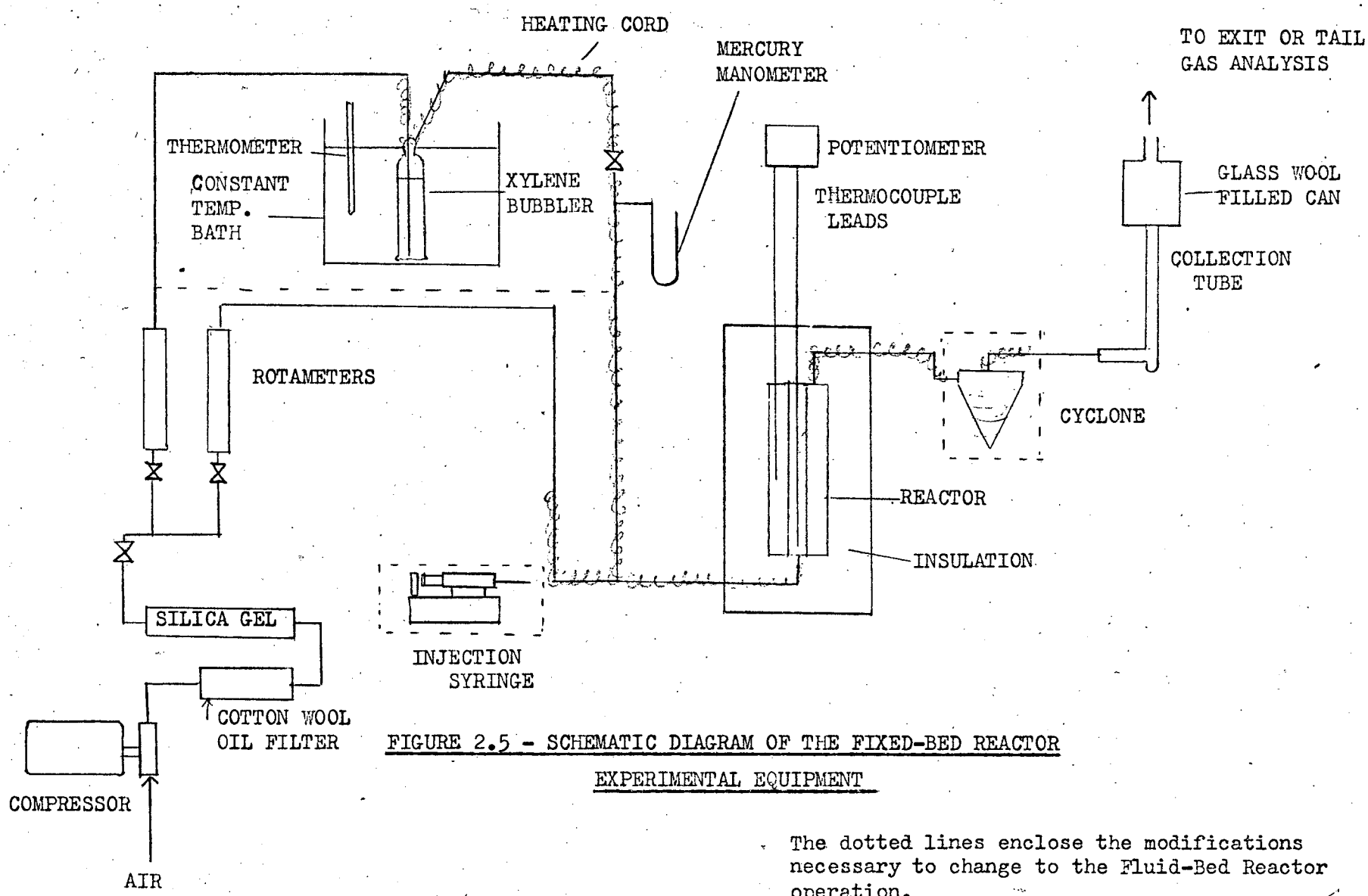


FIGURE 2.5 - SCHEMATIC DIAGRAM OF THE FIXED-BED REACTOR EXPERIMENTAL EQUIPMENT

The dotted lines enclose the modifications necessary to change to the Fluid-Bed Reactor operation.

2.2.1 Xylene addition

The xylene addition system was very similar to that used with the C.S.T.R. A larger bubbler of 700 ml capacity, with a one inch diameter sintered glass distributor was used.

The glass-to-metal joints at the bubbler were made using screwcap joints, similar to the Quickfit glass ones, but of stainless steel. Quickfit glass joints with machined metal caps were tried, but the threads on the glass tubes were of poor precision resulting in frequent breakage. Therefore, metal tubes were made, and these, when used with the Quickfit silicone and teflon rings, proved satisfactory.

2.2.2 The Reactor

The reactor is shown schematically in Figure 2.6.

It consisted of a cylindrical aluminium block, twelve inches long by six inches in diameter, with a two inch hole drilled through it. The lowest inch was drilled out further to $2\frac{1}{4}$ inches diameter to provide a ledge against which the sintered steel plate could be pressed. The plate was placed in an aluminium cup, asbestos gaskets placed above and below, and the cup pressed against the ledge by the bottom flange piece.

The top flange was sealed by using a copper-asbestos gasket.

A fine steel tube, 1/10 ich o.d., was positioned centrally in the reactor and soldered to the top flange plate. It reached to $\frac{1}{4}$ inch above the sintered base plate and a thermocouple could be moved along it to measure the axial temperature at any point. The block temperature was measured with a thermocouple placed in a hole drilled in the block two inches from the centre and eight inches deep. Another thermocouple was placed in this same hole to provide an input reading for the temperature control unit.

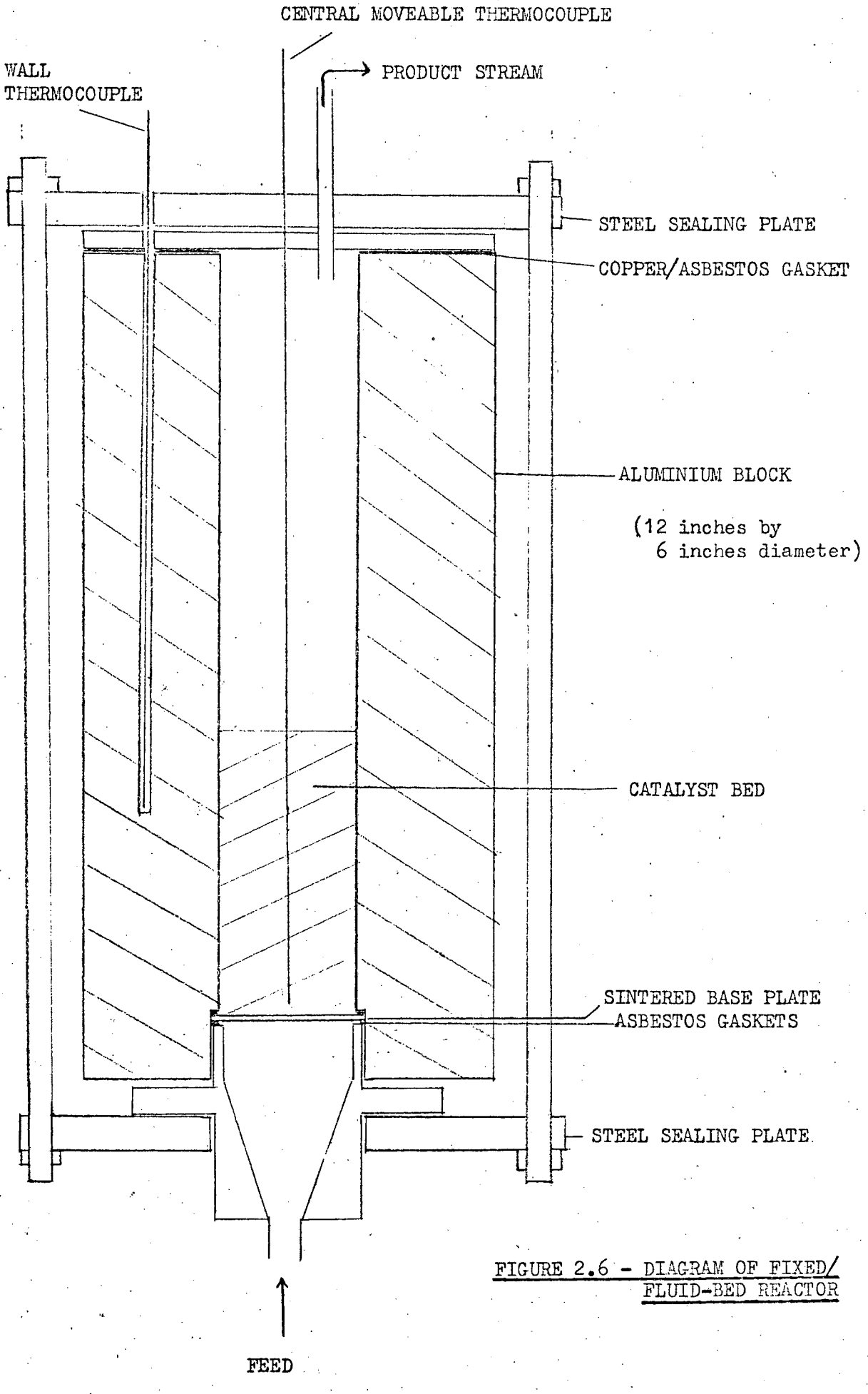


FIGURE 2.6 - DIAGRAM OF FIXED/FLUID-BED REACTOR

The block was heated via 150 ft. of 22 s.w.g. Toplet A resistance wire (0.83 ohm/ft at 20°C). The block was first surrounded by a layer of miconite to insulate it electrically from the wire, which was then wound on at eight turns per inch. The wire was then covered with alundum cement. A centre tapping was made to the wire to permit the wire to be used as either two heaters in series or in parallel.

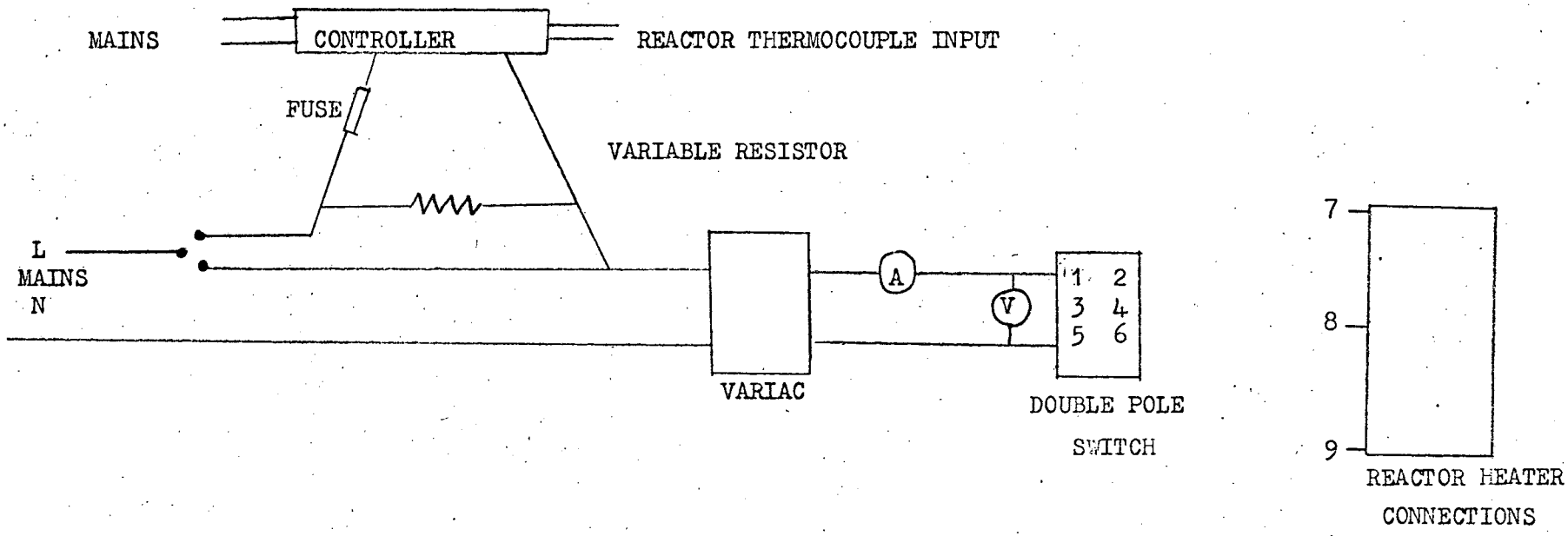
The temperature of the block was held to a set value by a Smiths Electrical Anticipatory Controller. The control circuit is shown in Figure 2.7. It was possible to have an input to the heaters of approximately 2 KW with the heaters connected in parallel; this was used to heat the block rapidly to reaction temperature from room temperature. However, as the Controller's relay contacts were rated at 4A, the controller was bypassed during rapid heating. When the block was near reaction temperature, the heaters were connected in series and the controller switched on. The current was usually then about 2A.

The controller initially operated as an on-off one, but it was found that the surge frequently blew the 3A fuse protecting the relay contacts. Therefore, the controller was connected in parallel with a small variable resistance, thereby lowering the surge from zero - 2A to approximately 1.6-2A.

The reactor block was contained in an asbestos box, 12 inches square by 30 inches high, filled with vermiculite (expanded mica) insulation. This was sufficient to reduce the outer surface temperature of the box to below 50°C.

2.2.3 Product Collection

The products were condensed out of the exit gas stream by passing them from the heated lines to an air condenser, one of the 'L'-shaped glass tubes.



DOUBLE POLE SWITCH CONNECTIONS

INPUT	L-3 N-4	OUTPUT a) SERIES HEATING	b) PARALLEL HEATING
		SWITCH 3-5 4-6	SWITCH 3-1 4-2
		TO REACTOR 5-7	TO REACTOR 1-8
		4-9	2-7
		6 unconnected	4-9

FIGURE 2.7 - FIXED-BED REACTOR HEATER CIRCUIT

As the electrostatic precipitator was of insufficient power to prevent all the solid mist from leaving the tube, it was not used, but instead a glass-wool filled can (three inches diameter by five inches long) was fitted to the end of the condenser. A slight loss of phthalic anhydride occurred initially until some phthalic anhydride crystals had been deposited on the glass wool. This took only a few minutes, and to minimise the effect of this loss, a collection lasted for one hour.

Not all of the exit xylene and probably not all of the exit tolualdehyde, was collected.

2.2.4 Analysis Equipment

The same equipment that was used for C.S.T.R. product analysis was also used here - see section 2.1.4.

2.2.5 Catalyst

The only catalyst used in the fixed-bed reactor was No. 1 - the same catalyst that Caldwell used. In all runs, it was diluted with the following inert material:

Supplier	: Norton Abrasives Ltd.
Catalogue No.	: S.A. 201
Size	: 3/16 inch diameter spheres
Composition	: Al_2O_3 - 90.4%, SiO_2 - 8.46, Fe_2O_3 - 0.26
	TiO_2 - 0.28, CaO - 0.04, Na_2O - 0.33, K_2O - 0.09
Apparent porosity	: 39 - 45%
Surface Area	: $< 1\ m^2/gm$
Apparent S.G.	: 3.5 - 3.7

These alundum spheres were not entirely satisfactory as some segregation occurred when mixed with catalyst, especially when pouring this mixture into the reactor.

The dilution ratio on all runs was three volumes of inerts to one volume of catalyst pellets; the reactor was changed with approximately 200 ml of mixture giving a bed of about four inches.

2.2.6 Chemicals

The chemicals used were the same as for the C.S.T.R. (section 2.1.6) except for the acetone; instead of 'Analar' grade, 'B.P.' grade acetone from A. and J. Beveridge, Edinburgh, was used.

2.2.7 Experimental Procedure

The reactor heaters and the constant temperature bath ran continuously. The reactor was kept at a temperature above 370°C. The controller set point was put to the desired block temperature at least two hours before a run, but usually the day before. The 'Thermotrace' line heating cords were switched on about ten minutes before a run. The product disposal system was then connected. A Quickfit 'L' tube (again coupling was done using glass ball joints and a machined metal cone) was connected to the reactor exit line; P.V.C. flexible tubing was then used to connect the glass tube to a one gallon capacity tin can, packed with glass wool. The exit gases from this can were vented to the outside atmosphere.

The gas flows were then turned on and adjusted to the required rates. The axial temperature profile was monitored by moving the thermocouple in the central steel tube. A virtual steady state profile was reached in about 30 - 40 minutes.

After one hour the collection condenser and glass wool filled can were connected in and a collection began. For the first few minutes a loss of product was apparent until a layer of phthalic anlydride crystals had been deposited on the glass wool. The loss then ceased. To minimise the error caused by this loss collections lasted for one hour.

As the collection proceeded, the pressure drop through the system rose and constant adjustment was necessary to the flowrates.

Tail gas analyses were made ten minutes after the start of a collection and five minutes before the end, by connecting a plastic T-piece to the exit of the condenser can. The gas analysers were connected to one limb of this and a restriction was applied to the exit limb to force a gas sample through the meters.

To prevent erroneous readings from, or damage to, the gas analysers, tail gas analyses were not performed unless the gas stream through them was phthalic anhydride-free so that there was no possibility of phthalic anhydride condensation in the meters.

Tail gas analyses were therefore performed only when the collection system was in use.

Depending on how long it took to set up the collection system again, a second collection was begun $2\frac{1}{2}$ - $2\frac{3}{4}$ hours after the run began. Two tail gas analyses were made during this collection.

To shutdown the reactor, the xylene input stream was turned off and the bypass stream left on for approximately two minutes to clear organic products from the reactor. Then the gas flow and the line heating cords were turned off.

The products collected were washed out of the condenser with several volumes of acetone, great care being taken to ensure a thorough extraction of products from the glass wool. In all, about two litres of acetone were used per sample.

The resulting solution was then analysed in the chromatograph as described in section 2.1.7. An agreement of within 8% between the amounts of phthalic anhydride in the two samples was considered sufficient and the average value taken.

2.3 The Fluidised-Bed Reactor Apparatus

The following changes were made to the fixed-bed equipment to enable the reactor to be run in the fluidised-bed mode:

2.3.1 Xylene Input

To fluidise the catalyst bed, a greater flowrate of air than had been used in the fixed-bed was desired. This was achieved by simply replacing the small rotameter with another 0 - 10 litres/min rotameter to allow the greater throughput. However, this meant that to maintain the same inlet concentration of xylene an increased xylene input was necessary. While this could have been achieved by the bubbler system, it was found more convenient to use direct xylene injection from a 'Meltec' Infusion pump fitted with a 50 ml glass syringe. In this device the syringe piston is driven forward at one of ten rates by a self-starting synchronous motor couple to a ten-speed gearbox, the speeds being selected by a switching knob.

The pump used in this work was a Model D.N./2 which came fitted with a 50 ml B-D disposable Plastipak syringe, giving flowrates in the range 0.13 - 133.3 ml/hr. The piston head of this syringe was covered by a rubber seal and so, to prevent possible swelling of this rubber by xylene with consequent impeded forward motion, glass syringes with glass pistons were used.

The method of injection is shown in Figure 2.8.a. It was done by injecting through a chromatograph septum fitted to a standard Ermetic T-piece. The airflow was preheated with thermocord before the injector.

2.3.2 Catalyst

The manufacturer of the fixed-bed catalyst did not make fluidising catalyst of the same composition. To enable meaningful comparisons of the results from the three reactors, it was decided to crush the fixed-bed pellets to a size suitable for fluidising. The assumption would then be made that since the pellets were surface-coated only, the catalytic area per unit mass would be unaltered.

The crushing was performed by the Apex Construction Co., Soho Square, London, in one of their stainless steel vibratory ball mills. They reduced the pellets to less than 100 microns diameter. A size analysis of the returned catalyst is given below.

wt % retained on sieve	mesh size
15	90 microns
17	75 microns
31	63 microns
27	45 microns

(The remainder passed through the 45 sieve)

A small cyclone was fitted to the reactor exit line to prevent catalyst being carried through to and beyond the collection condenser. The cyclone was made of aluminium, conical shape, five inches diameter by seven inches high. The gas entered tangentially and left through a tube located centrally through its top plate. A small bolt could be unscrewed from the bottom of the inverted cone to permit removal of catalyst. No provision was made for returning any such catalyst to the reactor.

The Analysis Equipment and Chemicals used were the same as for the fixed-bed rig (see sections 2.2.4, 2.2.6).

2.3.3 Experimental Procedure

The procedure was virtually identical to the fixed-bed reactor procedure (2.2.7) except for a slight discontinuity in the xylene input. Under normal operating conditions, a 50 ml syringe contained sufficient xylene for a run of approximately 1¾ hours. The first collection of one hour duration was therefore begun 40 minutes after the commencement of a run. When the syringe piston reached the end of its travel, a warning light on the pump came on. At this point, the syringe was removed, the piston driver returned to its initial position, another full syringe placed on the pump and the injection restarted. With practice, this could be done in less than thirty seconds. The second collection was begun forty minutes later.

2.4 Interconnection of the Fixed-Bed Reactor and the C.S.T.R.

On several occasions it was desired to feed either the fixed-bed product stream or the fixed-bed tail gas to the spinning catalyst-basket reactor inlet.

The product stream was so fed by the connection of 3/8 inch O.D. tubing from a T-piece immediately before the fixed-bed collection condenses to the 1/8 ich O.D. C.S.T.R. inlet line, normally used for the bubbler bypass flow. Seventeen feet of heated, lagged stainless steel tubing was required. The flow was directed along this line by the application of a restriction to the collection condenser exit. The flow was metered with a rotameter connected to the electrostatic precipitator exit.

Tail gas was fed to the C.S.T.R. from the collection condenser exit, via a nylon T-piece along nylon tubing to the inlet of the bubbler bypass rotameter and thence to the reactor.

Carbon dioxide-free tail gas was obtained by first passing the tail gas through a 250 ml bubbler containing solid sodium hydroxide pellets. The efficiency of this removal was checked with the carbon dioxide gas analyser.

2.5 Experimental Difficulties

Two major practical difficulties were encountered in this work - the collection of the exit xylene and the removal of leaks from the aluminium block reactor. Only the latter was satisfactorily resolved.

2.5.1 Xylene Collection Attempts

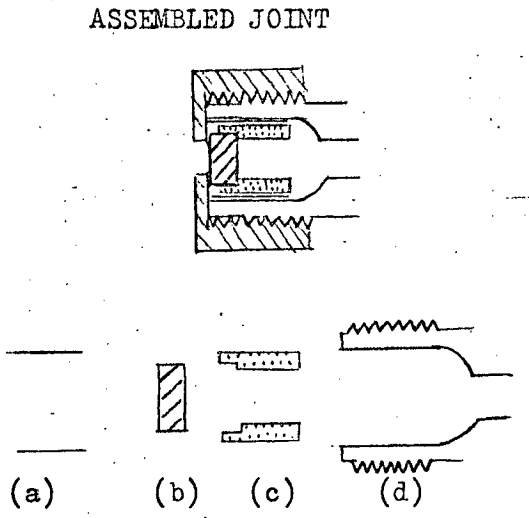
It was possible to check that the airstream passing through the xylene bubbler was being fully saturated by passing the stream through a water-cooled condenser, the exit gas temperature being measured. The xylene collected plus the xylene leaving the condenser in the air saturated at the exit temperature was found to equal (to an acceptable accuracy) the xylene leaving the bubbler in the air saturated at bubbler temperature.

Further details of this are given in section 2.6.7 on calibration.

Every collection system tried was connected to an eighteen inch long ¾ inch i.d. glass 'U'-tube, immersed in a mixture of acetone and solid carbon dioxide contained in a vacuum flask. This tube was loosely packed with glass wool.

The 'L'-shaped tube with electrostatic precipitator was able to collect approximately 60 - 70% of an exit xylene stream of 1% concentration. The vertical limb of the tube was then surrounded by a perspex cylinder (four inches diameter by nine inches high) packed with solid carbon dioxide. The xylene could be seen to solidify in the tube, but some revapourised when it reached the precipitator section which was uncooled. For safety reasons since the outer electrode was charged to 6000 volts, the cooling cylinder stopped one inch short of the bottom of the electrode. To improve heat transfer with the glass tube, the solid Co_2 was later replaced with liquid acetone chilled by solid carbon dioxide. The highest recovery recorded with this system on a 1% xylene stream was 85%. The best recoveries on lower concentration were less than this. In every run, a significant amount of xylene was found in chilled 'U'-tube after the collector.

It was impracticable to employ this 'U'-tube as part of the collection system since a disproportionately large volume of acetone was needed to wash thoroughly its large surface area and especially the glass wool, resulting in a very dilute solution for analysis. The acetone and xylene were two of the more difficult peaks to separate in the chromatograph columns; the xylene peak came just before the end of the tail of the acetone peak at the lowest practical temperature for analysis. The analysis of this very dilute solution of xylene in acetone would result in a larger acetone tail, a smaller xylene peak and a large baseline disturbance since higher amplification of the signals would be required.



(a) Compression ring

(b) Chromatograph Septum

(c) 3/8 " Steel tubing

(d) T-piece mouth

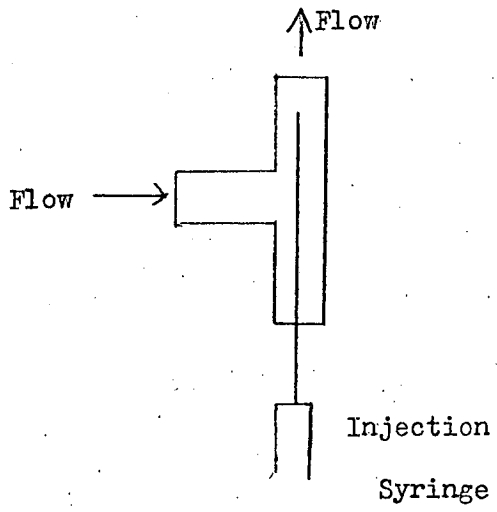
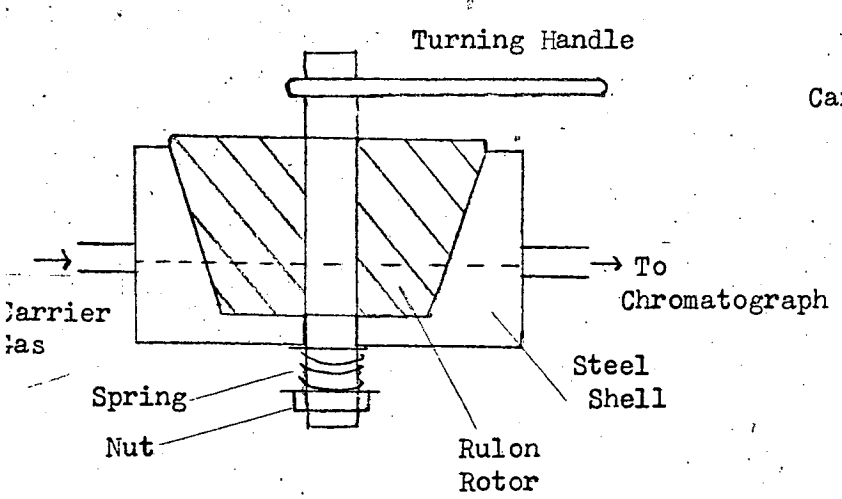
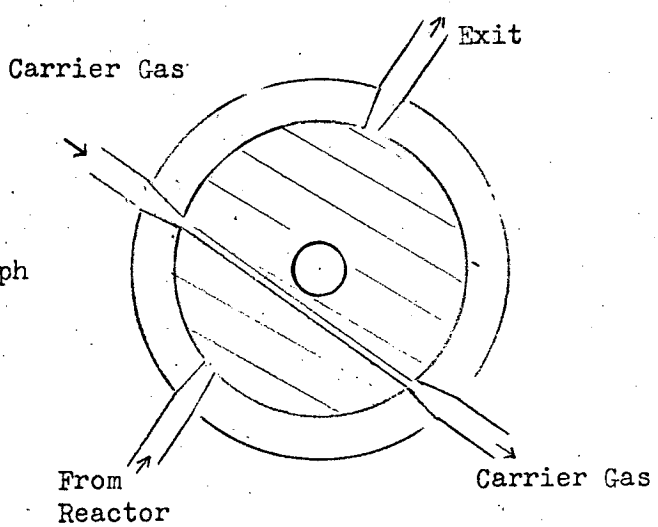


FIGURE 2.8a - o-XYLENE INJECTION METHOD

FIGURE 2.8b - GAS SAMPLING VALVE





The inaccuracy of this procedure was confirmed experimentally.

Attempts to adsorb the xylene on activated carbon were quickly abandoned after experimental trials showed that the carbon partially adsorbed other components as well (principally Co_2) and that the weight of carbon required was many times greater than the xylene to be adsorbed resulting in large weighing errors. And so, direct sampling of the product stream to the chromatograph was tried.

At that time, no supplier of suitable heated chromatographic gas sample valves was known, and so a valve was designed and then made in the Department workshop.

This valve is shown schematically in Figure 2.8.b It consisted of a conically-shaped rotor enclosed in a machined stainless steel body. By the rotation of this rotor through 90° a hole drilled through the rotor was moved from the direct path of one pipeline into the path of a second and at the same time sealed off the first. This hole was the sampling volume. The rotor had a steel shaft which passed through the steel body. The end of this shaft was fitted with a spring, the compression of which was designed to provide sufficient tension to seal the rotor into the steel body.

The rotor was first made from rulon (a glass-filled teflon), but soon after its introduction solid products were inadvertently allowed to condense at the junction of the rulon and steel body. (The heating to the valve was provided by wrapping thermocord round the steel body). On the next turn of the rotor some of this solid was carried round between the rulon and steel faces, scoring the rulon rotor and breaking its seal. The rulon rotor was then replaced with one made of Sindanyo asbestos.

The results from this valve were promising but not completely satisfactory. To maintain a surface seal, the spring had to be compressed to such an extent that movement of the rotor required great force. This meant that the sample could not be introduced instantly to the chromatograph nor without a disturbance to the flow. Severe peak tailing and poor reproducibility were found.

A commercially-made valve was then obtained from Varian Associates, London. This valve consisted of a stainless steel cylinder (approximately two inches x $\frac{3}{4}$ inch diameter) to which the product lines and carrier gas lines were attached. The sample loop ($\frac{1}{2}$ ml) connected to the cylinder body via two compression nuts. Heating was achieved via a 20 watt cartridge heater inserted in a rectangular steel block welded to the cylinder body at right angles to the sample loop. The movement of a piston (with five sealing rings along its length) within the cylinder permitted the loop to be filled by the product stream while carrier gas bypassed the loop or the loop to be emptied into the chromatograph by the carrier gas while the product stream bypassed.

As the heater provided with this valve is far removed from the sample loop it was necessary to heat the loop with thermocord and insulate it with asbestos.

This valve gave unsatisfactory results. The peaks obtained were of very poor reproductibility and considerably smaller than they should have been. Direct sampling of a xylene stream of known composition gave peaks often below 50% of the value obtained by an injection of the same amount. Investigation showed that the xylene was being absorbed by the sealing rings, which were soon swollen, softened and broken in use.

The five different types of ring that Varian could supply (viton, buna N, neoprene, silicone and kel F) were all tried and none were satisfactory. They absorbed some of the xylene and/or were unable to be operated for any length of time at the required temperatures (150°C). The use of the Kel F rings suggested that phthalic anhydride was also being partially absorbed on the others.

At this time oxygen and carbon dioxide analysers were obtain and as a considerable time had already been spent fruitlessly on xylene collection, it was decided to press on with kinetic runs, the exit xylene being calculated by a mass balance.

2.5.2 Sealing the Fixed-Bed Reactor

Although this reactor could be sealed at room temperature, severe leaking was found to develop as the block temperature was raised caused by the loosening of the steel bolts which turned in their tappings, thus releasing the pressure on the flange plates.

It was not possible to tighten these bolts at reaction temperature since, with the verniculite insulation and one side of the asbestos box removed, the heaters were capable of raising the block temperature to only 330°C. The top and bottom flange bolts were normally retightened at this temperature and then with the insulation replaced, the temperatures raised. The top bolts could still be retightened at the higher temperatures used, since rapid access to them could be got by the removal of a small amount of insulation, whereas rapid access to the bottom bolts was not possible.

Finally, after trials of many different gasketing materials etc., two mild steel plates ($\frac{1}{2}$ inch thick and 8 inches diameter) were cut and the necessary holes drilled through them to permit the passage of the inlet and exit lines.

These two plates, linked by three screwed rods, were placed one pressing down on the top flange, the other pressing up on the bottom. The intention was to permit an increase of pressure to be applied to the bottom flange piece by tightening the rods from the top. It was found that a better seal could be achieved if the rods were tightened at room temperature, then, as the temperature was raised, the faster expansion rate of the aluminium ensured that the block expanded into the two steel plates, giving an excellent seal.

2.6 Calibration Procedures

2.6.1 Rotameters

The small rotameters (below 700 ml/min) were calibrated for air and where necessary for nitrogen and/or oxygen, by the use of a soap bubble meter and by water displacement.

The two larger rotameters used on the fluidised-bed rig were calibrated with a wet gas meter.

On two occasions it was desired to introduce carbon dioxide to the C.S.T.R. The only rotameter of small enough range was the shaft purge rotameter. Since the carbon dioxide reacted with the soap solution in the soap bubble meter, this rotameter was connected in parallel with an already calibrated air rotameter. The carbon dioxide gas analyser was then used to measure the CO_2 concentration in the mixed stream.

2.6.2 Thermocouples and Thermometers

All the thermocouples used were nickel-chromel/nickel-alumel and were checked to 350^{o}C against standard thermometers which were accurate to within 0.1^{o}C. No standard thermometers were available above this temperature.

The thermocouples were checked by placing them in a specially drilled brass block along with a standard thermometer, contained in a heated Pyrex flask and surrounded by alumina pellets (the same type as were used as a catalyst diluent). The thermocouples were within 1.5° of the true reading at 350°C, the temperatures being read with a Longscale potentiometer itself accurate to only 1°.

The thermometers were checked in the constant temperature bath against the same standard thermometers.

The corrected temperatures are used throughout this study.

2.6.3 Tachometer

The reed relay and tachometer were calibrated using a stroboscope to find the rotational speed of the outer magnet drive unit, which is the same as the shaft speed. The majority of the runs in the C.S.T.R. were performed at a true shaft speed of 3000 r.p.m.

2.6.4 Gas Analysis Equipment

The Grubb Parsons Infra-Red Gas analyser was factory calibrated for carbon dioxide in the concentration range 0-10%. A daily check could be obtained by setting the instrument zero using CO_2-free nitrogen and then operating a solenoid switch which caused a wire to be moved into the optical path. A potentiometer could be then adjusted to give a prespecified wire reading.

Two methods were used to check the factory calibration graph. In the first, an air and carbon dioxide rotameter were connected in parallel, and, using Rotameter Co.. calibration charts, the mixed flow was passed through the analyser.

In the second, a glass flask of known volume, covered with a rubber seal, was filled with nitrogen. A known volume of carbon dioxide was injected into the flask through the rubber, with a Plastipak disposable syringe. The contents of the flask were thoroughly mixed by prolonged shaking (pieces of wire gauze were put in the flask to increase the turbulence) and then 50 ml of mixed gas withdrawn with another Plastipak syringe, and this volume passed through the analyser sample cell.

Both methods confirmed the factory calibration graph. However, after several months use, the check wire turned on its mounting, necessitating a new wire value to be specified. This new value was checked once a fortnight using the flask/injection method, to ensure no further movement of the wire.

The analyser was unaffected by water vapour, carbon monoxide or xylene. A sample of tail gas which had been passed through the sodium hydroxide bubbler gave a zero reading, indicating that none of the other components present in this stream caused any interference.

The Servomex oxygen analyser makes use of a paramagnetic susceptibility measuring cell and has a range of 0-100% oxygen on a 3600° (ten-turn) linear dial graduated to 0.1%. The linearity of this device was checked with a digital voltmeter connected across the output terminals of the cell and was found to be better than 0.1% oxygen.

The mechanical zero of this device was set using oxygen-free nitrogen and the span adjusted to read 99.70% oxygen on B.O.C. cylinder oxygen. This gave a reading of 20.95% oxygen in dry air. The zero point and span reading were checked daily.

This device gives a reading of the volume % of oxygen in the sample cell, so, for a mass balance account must obviously be taken of the other components (e.g. CO_2, H_2O) present, but none of these has a significant magnetic susceptibility.

2.6.5 Leak Tests

The C.S.T.R. was pressure tested daily. It was required to hold a pressure of 3 cm. mercury gauge unaltered for three minutes at reaction temperature. Whenever the bubbler was refilled or the catalyst changed, a test of 6 cm. was applied for the same time. The maximum pressure in this system during operation never exceeded 2 cms.

The fixed/fluidised-bed reactor was never made completely leakfree. If however, at reaction temperature, the pressure fell from an initial 10 cms. mercury gauge by less than one cm. over three minutes, the test was considered satisfactory. The pressure in this system gradually rose during product collection to a maximum of approximately 5 cms.

2.6.6 Chromatograph

The expected products - xylene, o-tolualdehyde, o-toluic acid, phthalide, phthalic anhydride and maleic anhydride (dissolved in acetone) - and naphthalene were analysed separately and together to check for possible interference of the peak areas. Naphthalene was used as an internal marker to permit more accurate analyses since it gave a peak on the chromatograph trace well separated from the product peaks.

The integrator was set to cut on and off at a signal value of 1% of the full scale deflection value of the recorder to minimise the effect of small baseline disturbances and peak tailing.

Excellent straight lines were obtained for all the products; these did not pass through the origin since a finite amount of substance was required to give a signal greater than 1% f.s.d. to permit integration to begin.

The best resolution of the products was obtained from a column coated with 2-cyanoethyl methyl silicone on AW-DMCS chromosorb G. Although this column gave baseline drift, it was markedly superior to the one recommended by Perkin-Elmer for the required separation and still superior to a new column of the same nominal specification. This first column had been used for several years for the separation of naphthalene oxidation and ammoxidation products, and it appears that its history had significantly improved its ability to resolve the desired substances. The baseline drift was eliminated by balancing the column with a new column of the same specification, but analyses were done exclusively in the old column.

2.6.7 Xylene Input

The Xylene vapour pressure data available from the literature are in good agreement. The data of Stull[47], Perry et al[48], Waring et al[49] and Rossini et al[50] are plotted in Figure 2.9.

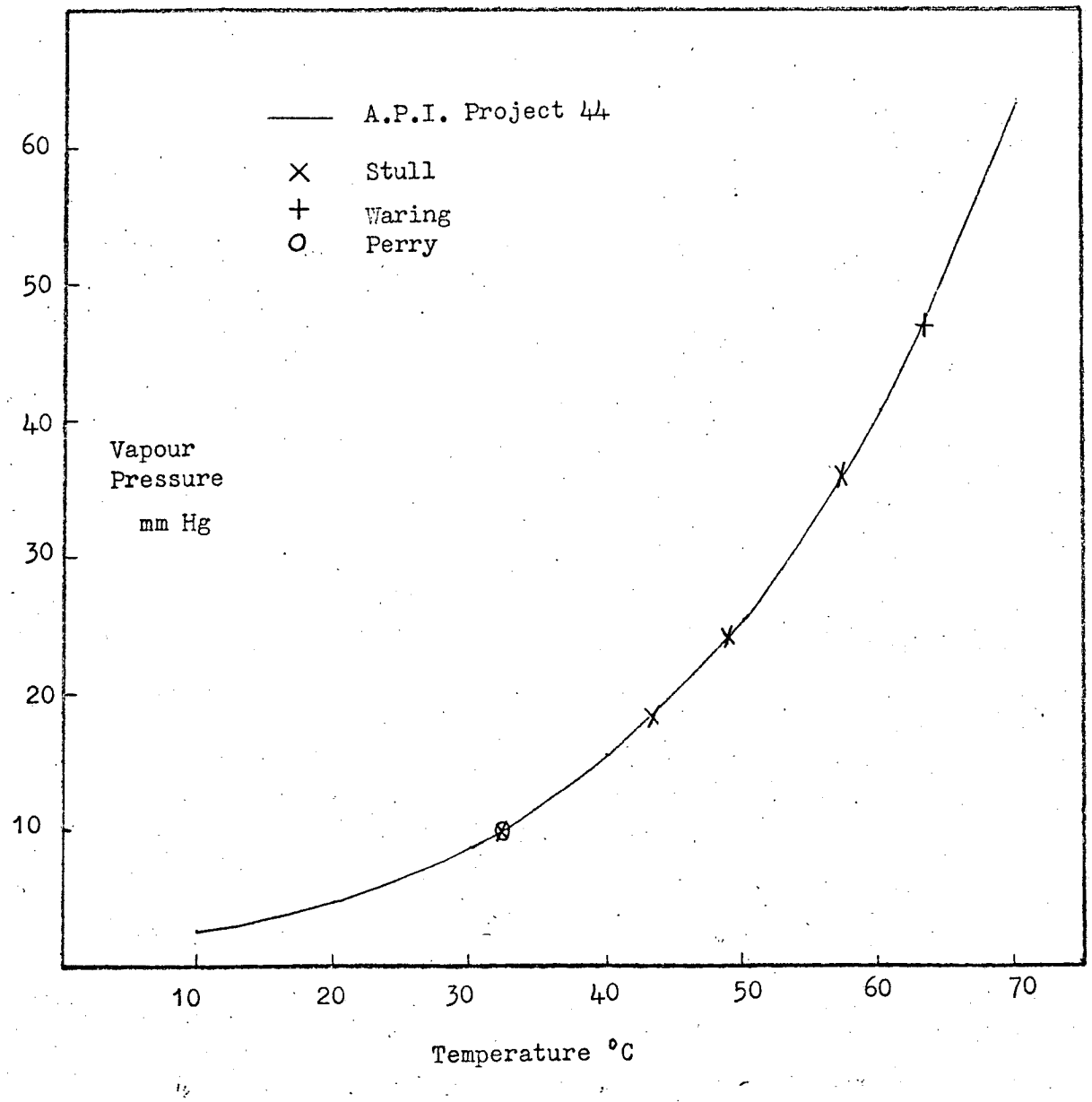
The equation presented by the last of these in API Research Project 44 was used throughout to calculate the vapour pressure. It is the Antoine equation:

$$\ln P = 6.99891 - (1474.679)/(213.686 + T)$$

where P is in mm Hg, T in ^{o}C.

A later review article by Gallant[51] contains a graph of o-xylene vapour pressure VS temperature which gives values consistently about 5% lower than the above equation. In the range with which this work is concerned (i.e. vapour pressures up to the normal boiling point) Gallant cites Stull[47] as the source of the data, whereas Stull's data in fact agrees with the above equation.

FIGURE 2.9 - o-XYLENE VAPOUR PRESSURE



It is presumed that Gallant's graph has been badly printed with a slight displacement of his linear plot. A letter to this effect was sent to Gallant but no reply received.

It was obviously important to ensure that the airstream passing through the xylene bubbler was being saturated with o-xylene. Since the exit xylene could not all be collected, the following method was used. A glass water-cooled condenser was connected to the reactor exit line, the line temperatures being between 100-150°C. Air was passed through the bubbler (at temperatures greater than 35°C), through the reactor system and into the condenser (at less than 12°C), and its temperature measured at the exit of the condenser. The xylene which collected in the condenser was dissolved in acetone and quantified chromatographically. The assumption was then made that the air leaving the bubblerwas saturated at bubbler temperature, and that the air leaving the condenser was saturated at exit temperature. Using the above Antoine equation, the recovery was then calculated.

Using the extreme flowrates and bubbler temperatures that were expected to be used in the kinetic runs ten xylene collections were made on the C.S.T.R. rig. These ten runs were then repeated with a bubbler liquid level of 75% of the first (full) value. All twenty recoveries were in the range 94-103%.

Similar runs were performed on the fixed-bed bubbler system, with the condenser connected directly to the bubbler exit. Ten runs only were made, and these had recoveries in the range 92-101%; no significant difference was apparent in the five runs performed with the lower liquid level.

The wide range of recoveries is believed to be due to the inherent inaccuracies of the collection procedure.

As will be discussed more fully later, the metering equipment used is believed to be of greater accuracy than suggested by these results.

The 'Meltec' Infusion pump, used for most of the fluidised bed runs, had ten precalibrated pumping rates; these applied only when a 50 ml B-D Plastipak syringe was used. These rates were checked by measuring the forward movement of the piston pusher with a 0-75 'thou' clock gauge and a stop watch. The multiplication of these rates by the measured cross-sectional area of a Plastipak syringe gave all the precalibrated rates within 0.75%. The input rates using the glass syringe were got by scaling these precalibrated rates with a factor equal to the ratio of the glass and plastic syringes cross-sectional areas.

Chapter 3

The Spinning Catalyst-Basket Reactor Oxidation Results

It should be borne in mind that when a stirred reactor is being operated at conversions greater than ~10%, the normal kinetic procedure of varying one reactant concentration while the others are held constant is not practicable unless a very rapid product analysis is possible. (Even then, successive alterations of the inlet conditions will disturb the system from the steady state and greatly lengthen runs). When the reaction is at steady state the inlet concentrations are immediately changed to the actual reactor concentrations which can be very different from those at the inlet.

The analysis system employed in this work took considerable time, and therefore it was not possible to vary the xylene and oxygen concentrations systematically. Therefore the data obtained has to be considered as a whole.

The concentrations measured and reported in this chapter are all the actual reactor concentrations.

3.1 Experimental Measurements

The following quantities were measured directly during experimental runs: the weight of o-tolualdehyde, phthalide, and phthalic anhydride leaving the reactor during a timed collection; the concentrations of carbon dioxide and oxygen in the tail gas; inlet gas flows to the reactor and bubbler; the temperatures of the bubbler, reactor and the laboratory; atmospheric pressure; the weight of catalyst in the basket; the basket rotational speed; the duration of each run; and the pressure drop through the system.

As will be discussed later, traces of o-toluic acid and maleic anhydride were frequently found, but were never of sufficient size to permit quantification.

By means of a mass balance (as described fully in Appendix 1) the following were calculated: the inlet flows (moles/min) of oxygen; nitrogen, o-xylene; the outlet flows of oxygen, nitrogen, o-xylene, o-tolualdehyde, phthalic anhydride, phthalide, carbon dioxide, carbon monoxide, and water; the outlet (reactor) concentrations of xylene, oxygen, carbon dioxide and phthalic anhydride; the rate of disappearance of xylene; the rate of appearance of phthalic anhydride and carbon dioxide; the percentage of inlet xylene that had reacted to carbon monoxide; and the moles of oxygen consumed per mole of xylene oxidised.

3.2 Estimation of Errors

Since the exit xylene concentration and the rate of xylene disappearance were not directly measured, but calculated by a mass balance, an overall estimate of the errors in the experimental equipment is difficult.

However, an estimate of the constituent errors which make up the total error, and hence the error in the calculated xylene concentration, may be obtained by reference to the work of Ross[31], who used the same reactor and similar metering, collection and analytical systems in his study of naphthalene oxidation. He performed a series of runs with no catalyst present and at temperatures where homogeneous combustion was negligible and found that the naphthalene collected in his electrostatic precipitator and quantified chromatographically was within $\pm$ 1.5% of the napthalene fed to the reactor calculated from the measured gas flows and bubbler temperature.

He concluded that it was probably a good assumption that no error greater than 1.5% existed in his measured data arising from errors in the estimated naphthalene concentration.

Since the system used in this study was so similar to Ross's and the measuring equipment was calibrated to at least the same precision, it would be unreasonable to assume that the errors in it are significantly greater than his.

This gives the following errors:

flow rates (oxygen, nitrogen, air)	$<= \pm 1.5\%$
weight of phthalic anhydride	$<= \pm 1.5\%$
weight of tolualdehyde	$<= \pm 5.0\%$
weight of phthalide	$<= \pm 5.0\%$
xylene inlet flow (calculated from bubbler temperature and gas flows)	$<= \pm 1.5\%$

The tolualdehyde and phthalide figures have been increased since they were present generally in small amounts with a resulting higher analysis error; in some runs the error will be even greater as they were found in concentrations too small to be quantified.

The error in the oxygen concentration may be taken as the reading error $\pm$ 0.05% oxygen, which will give, if it is assumed that the total flow remains constant and the inlet concentration is 21%, the following errors in the consumed oxygen:

$\pm$ 2.5% at an outlet concentration of 19%

$\pm$ 1.0% at an outlet concentration of 16%

Although the reading error in the CO_2 analyser is small, the calibration performed on this analyser agreed with the factory calibration graph to only ± 5% at 5% concentration of CO_2, and to 2% at 8% concentration. These figures will be taken as the CO_2 analysis error. If we consider a run with the following conditions,

inlet xylene concentration	1.5%
conversion	65%
selectivity to phthalic anhydride	40%
selectivity to other organic products	10%

the outlet xylene concentration will be approximately 0.5%. The following errors may be expected:

the reacted xylene	$<= \pm$ 4%
outlet xylene concentration	$<= \pm$ 12%
xylene disappearance rate	$<= \mp$ 6%

At higher outlet xylene concentrations the errors will be less, and conversely at lower concentrations. It is worth noting that if, for example, the errors lead to the outlet xylene concentration being underestimated, the xylene disappearance rate calculated from the difference in inlet and outlet concentrations, will be overestimated; this will result in rates that are too high being thought to have occurred at concentrations that are too low.

The total error in each run may be estimated in another way. This error will cause a deviation in the measured oxygen outlet concentration from the oxygen outlet concentration calculated from inlet conditions and the oxygen consumed in the formation of the collected organic products and the measured carbon dioxide.

To ensure a mass balance, the amount of xylene which would have to react to carbon monoxide to consume this oxygen "deviation" was calculated. For two reasons, one would expect a negligible carbon monoxide formation in this system:

a) the work is being performed using high temperatures, long residence times, an oxidation catalyst and a large excess of oxygen, and so one could reasonably expect the carbon monoxide to combust to carbon dioxide.

b) Trimm[40], in his study of air oxidation (and higher oxygen concentrations) of benzene in a similar reactor found no carbon monoxide in the exit gas.

Therefore, the magnitude of the carbon monoxide formation term may be taken as an estimate of the errors in the system. Typical examples will be discussed later when the runs have been discussed quantitatively.

3.3 Homogeneous Combustion of o-Xylene

A series of experiments was performed to determine the significance of xylene homogeneous reaction. The results are presented in Figure 3.1, and show that, at the conditions used in this study, the homogeneous reaction is negligible. Even at 450°C, 18° above the highest temperature used in this study, the homogeneous conversion is less than 5%. Catalytically, at 450°C, conversions of over 90% were obtained at similar conditions.

No condensable organic products were found in these runs; apparently, carbon dioxide was the only product.

3.4 Time Required to Reach Steady-State Conditions

The results from a series of runs carried out early in the study, before the carbon dioxide analyser was obtained, show that steady-state conditions were reached within an hour at 403°C. These results are shown in Figure 3.2.

3.5 Effect of Materials of Construction

The effect of the stainless steel was investigated by placing in the basket, beside the catalyst, stainless steel turnings and repeating a kinetic run. To investigate the effect of the nickel mesh, a circular layer of mesh was wound round the cruciform basket in addition to the normal mesh. The results are presented in Appendix 3, and show that an increase in the materials of construction had no measurable effect on the reaction variables.

3.6 Effect of Basket Rotational Speed

The results of this investigation will be discussed later in section 4.5, on mass transfer effects, but no difference was found, at 411°C and 432°C in runs performed at 2000 r.p.m. and 3800 r.p.m. At very low rotational speeds (less than 700 r.p.m.) results of poor reproducibility were obtained. A speed of 3000 r.p.m. was normally employed.

3.7 The Oxidation Results

The experimental results from the spinning catalyst-basket reactor are presented fully in Appendix 2. Plots of the calculated rate of xylene disappearance versus the calculated outlet (reactor) xylene concentration and versus the measured outlet (reactor) oxygen concentration are presented in Figures 3.3 - 3.10, for each of the four temperatures used in this study - viz. 391, 399, 411 and 432°C.

FIGURE 3.1 - HOMOGENEOUS COMBUSTION of o-XYLENE

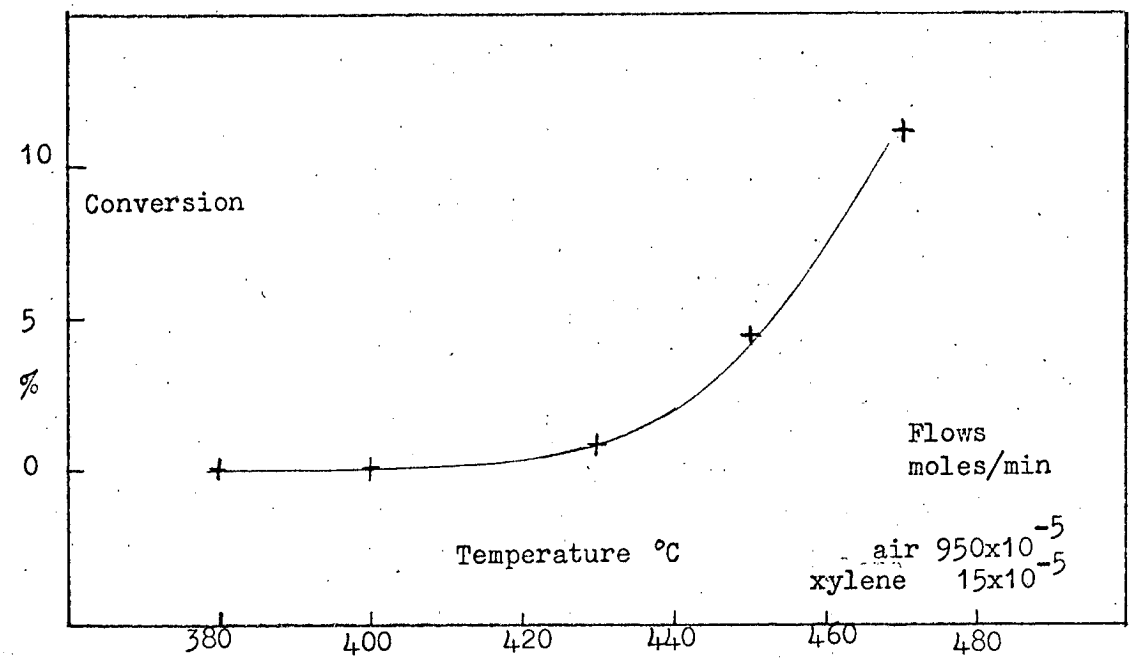
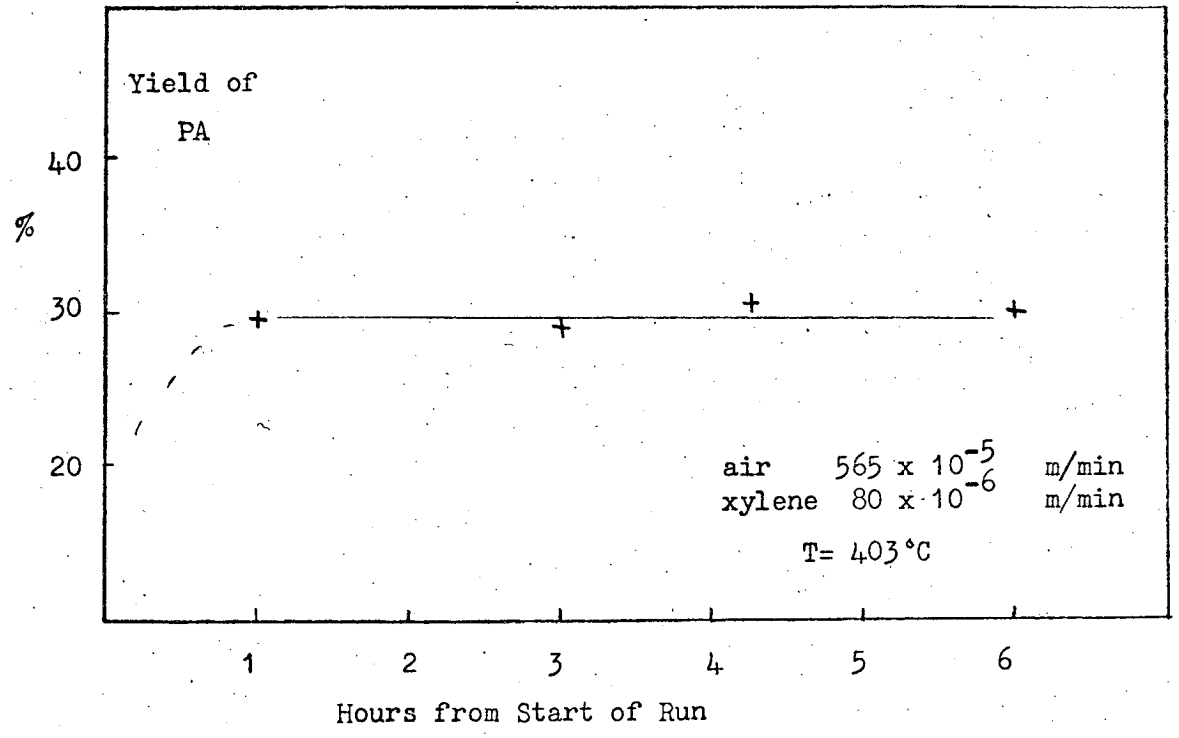


FIGURE 3.2 - Yield versus Start of Sample Collection



The xylene disappearance rate is discussed more fully and quantitatively in the next chapter. This section, and the remaining sections of this chapter, consist of the conclusions that may be drawn from a qualitative inspection of the results and of the tests performed to investigate the significance of various factors.

3.7.1 Xylene Disappearance Rate

An inspection of Figs. 3.3 - 3.10 suggests a strong dependance of the rate on the xylene concentration, but the magnitude of the oxygen dependency is not immediately obvious.

At each temperature, however, there are certain points on the xylene concentration graphs which are separate from the general trend:

a) at 391°C, two runs at fairly high xylene concentration have virtually zero rate.

b) at 399°C, two runs have rates below the general trend, one at the highest xylene concentration, the other at an intermediate value.

c) at 411°C, there are eight points which appear to exhibit the same trend as the others, but have considerably higher rates.

d) at 432°C, five runs performed at very high xylene concentration have rates much lower than would be expected from an extrapolation of the rates of the remaining points.

These points, seventeen in total, are not distinguishable from the other points by means of their oxygen concentrations or indeed, as will be discussed later, by any other concentration.

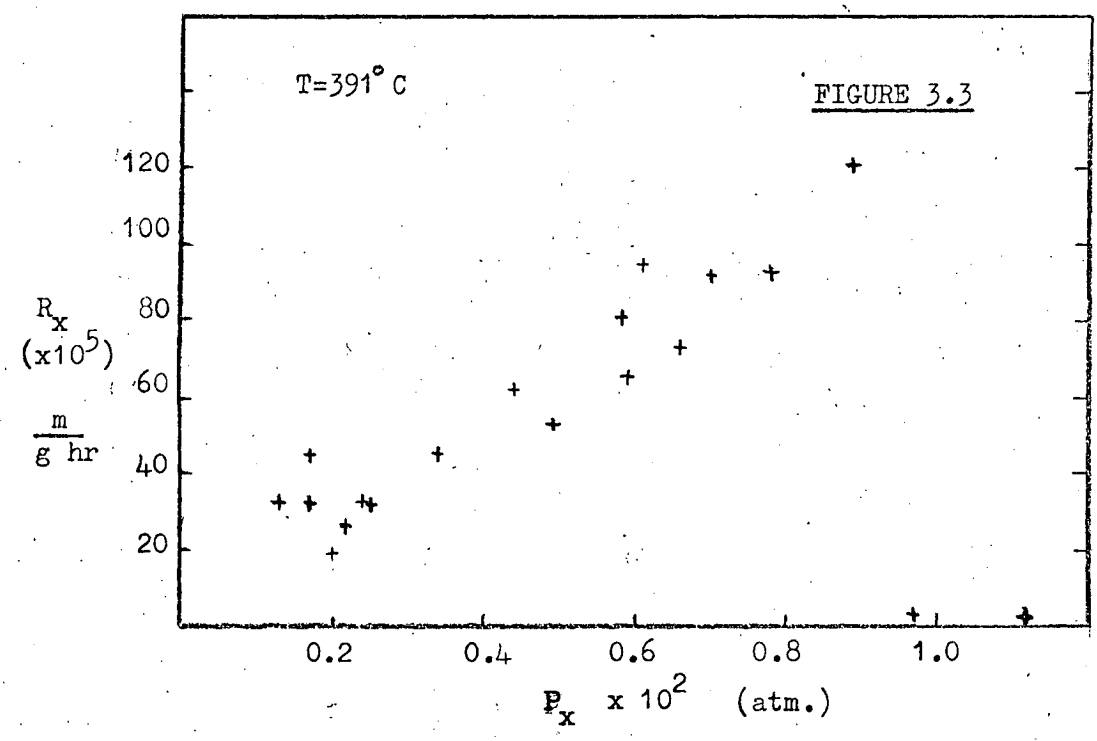


FIGURE 3.3

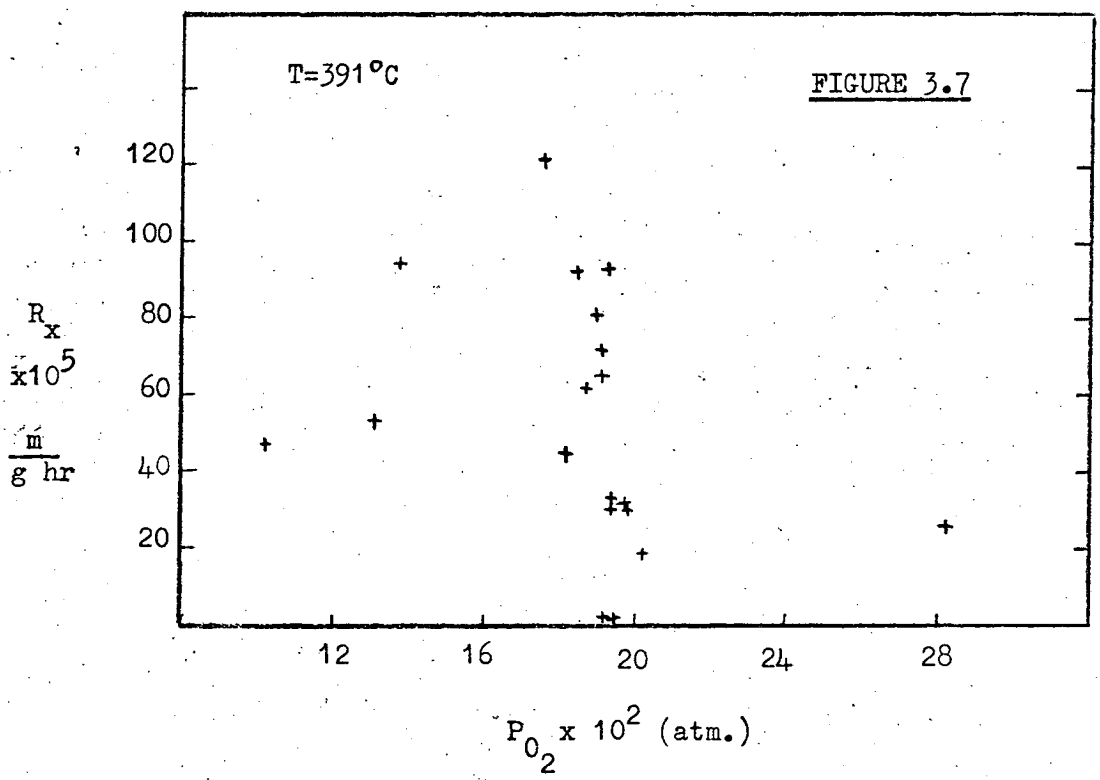


FIGURE 3.7

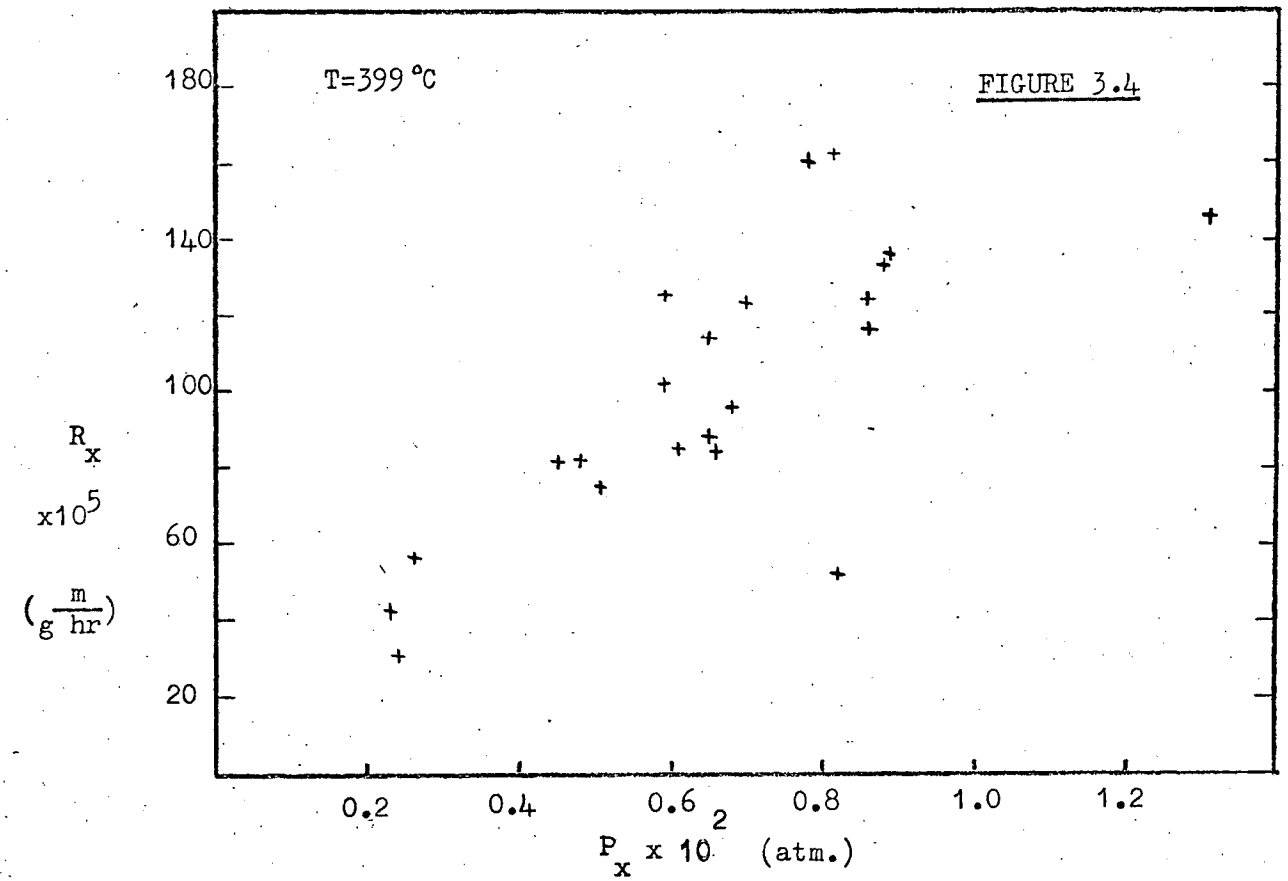


FIGURE 3.4

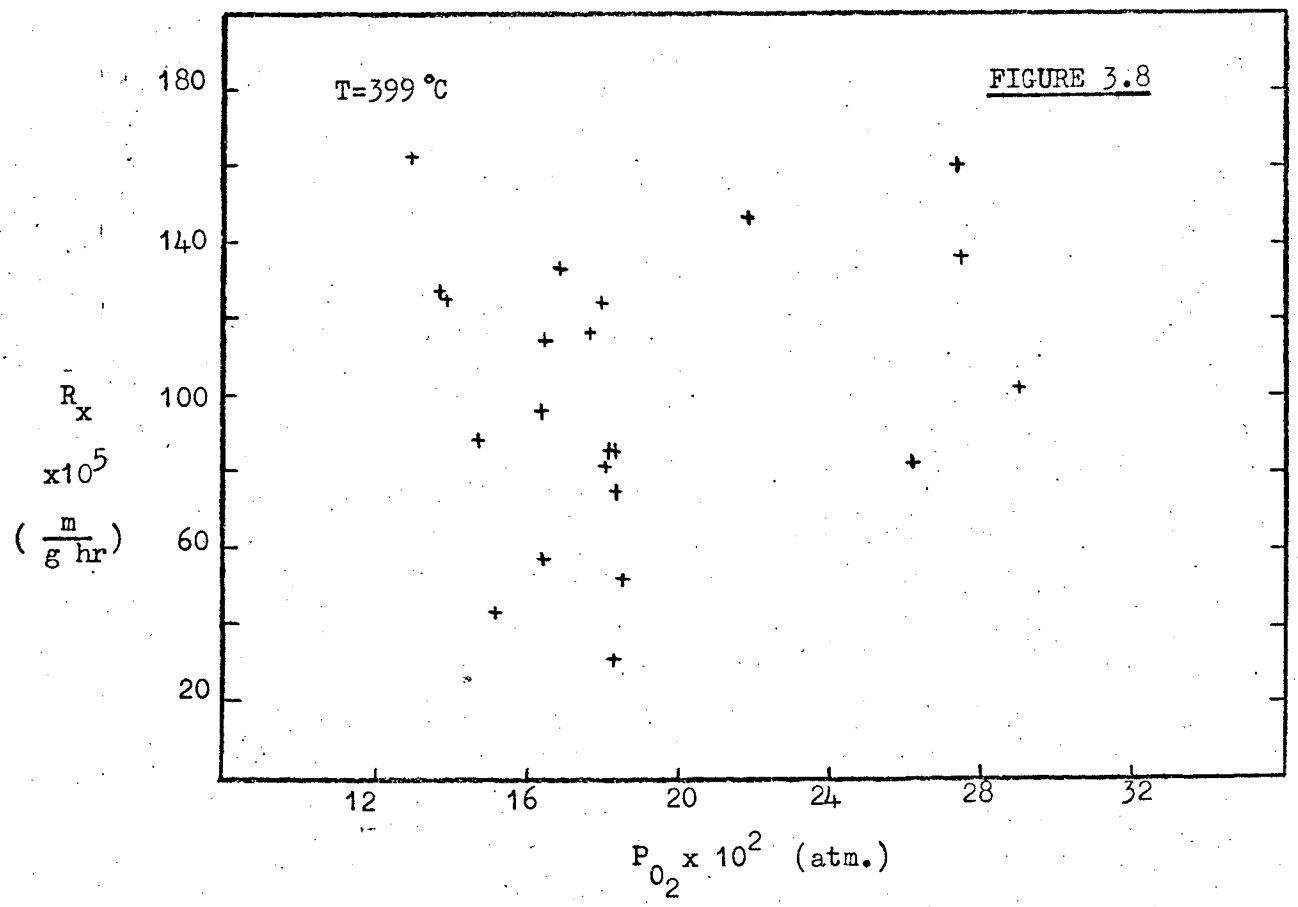


FIGURE 3.8

FIGURE 3.5

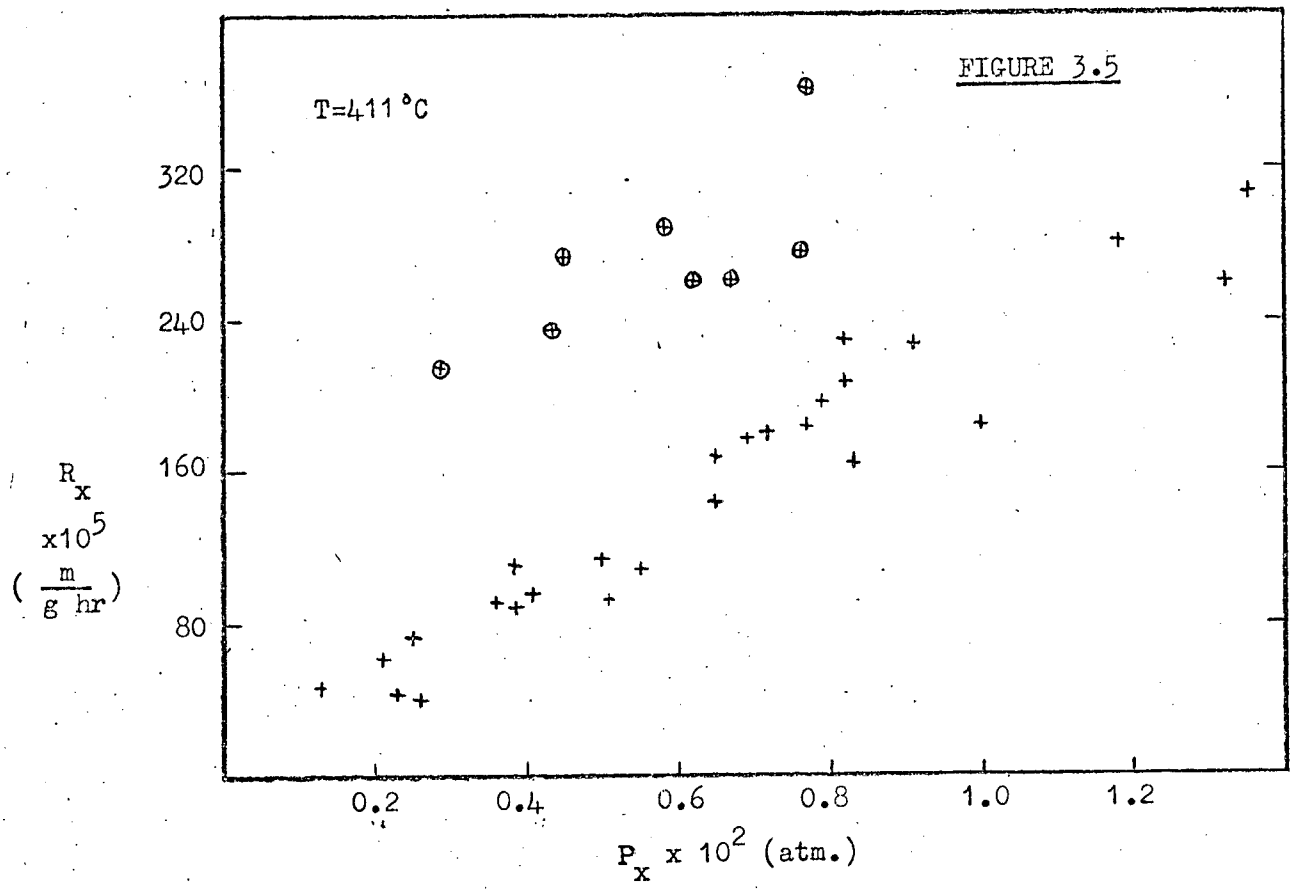


FIGURE 3.9

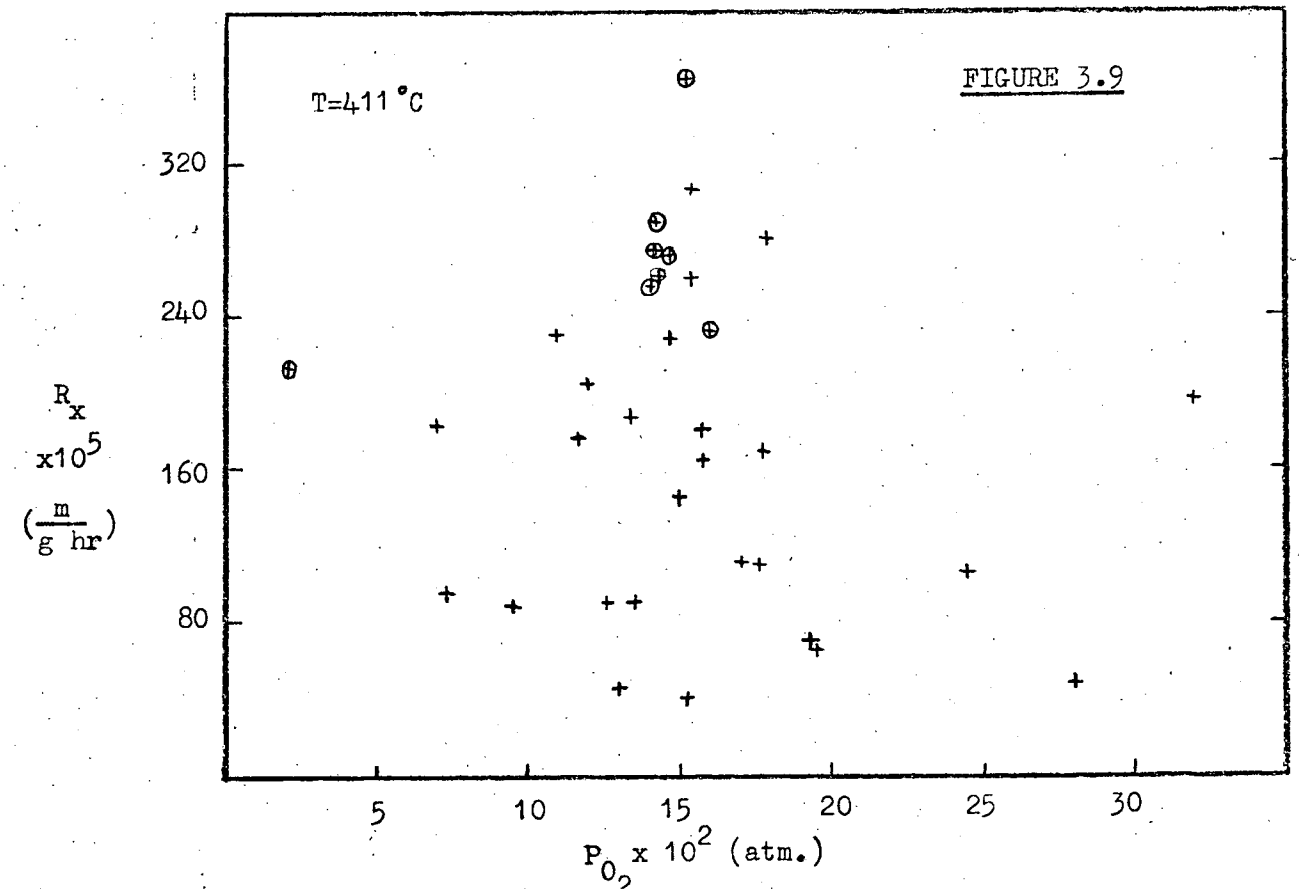


FIGURE 3.6

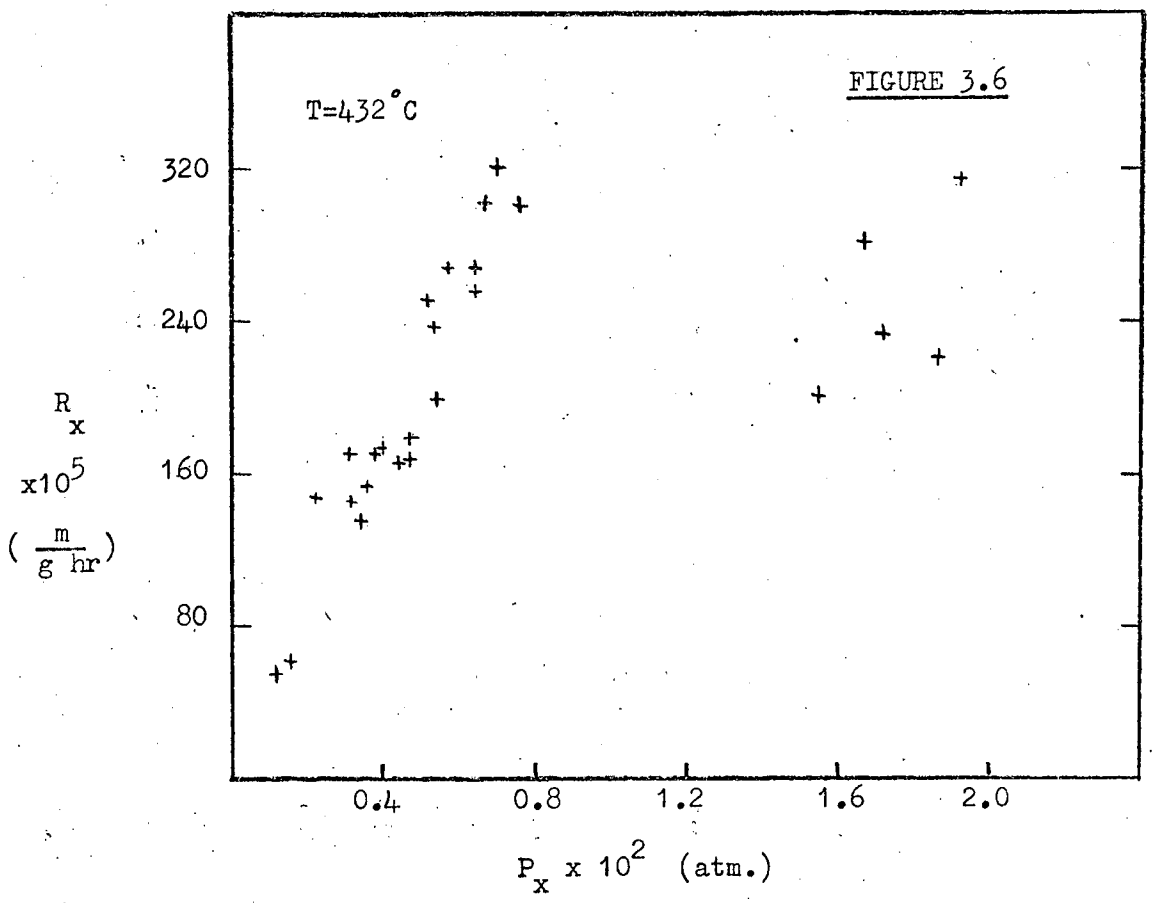
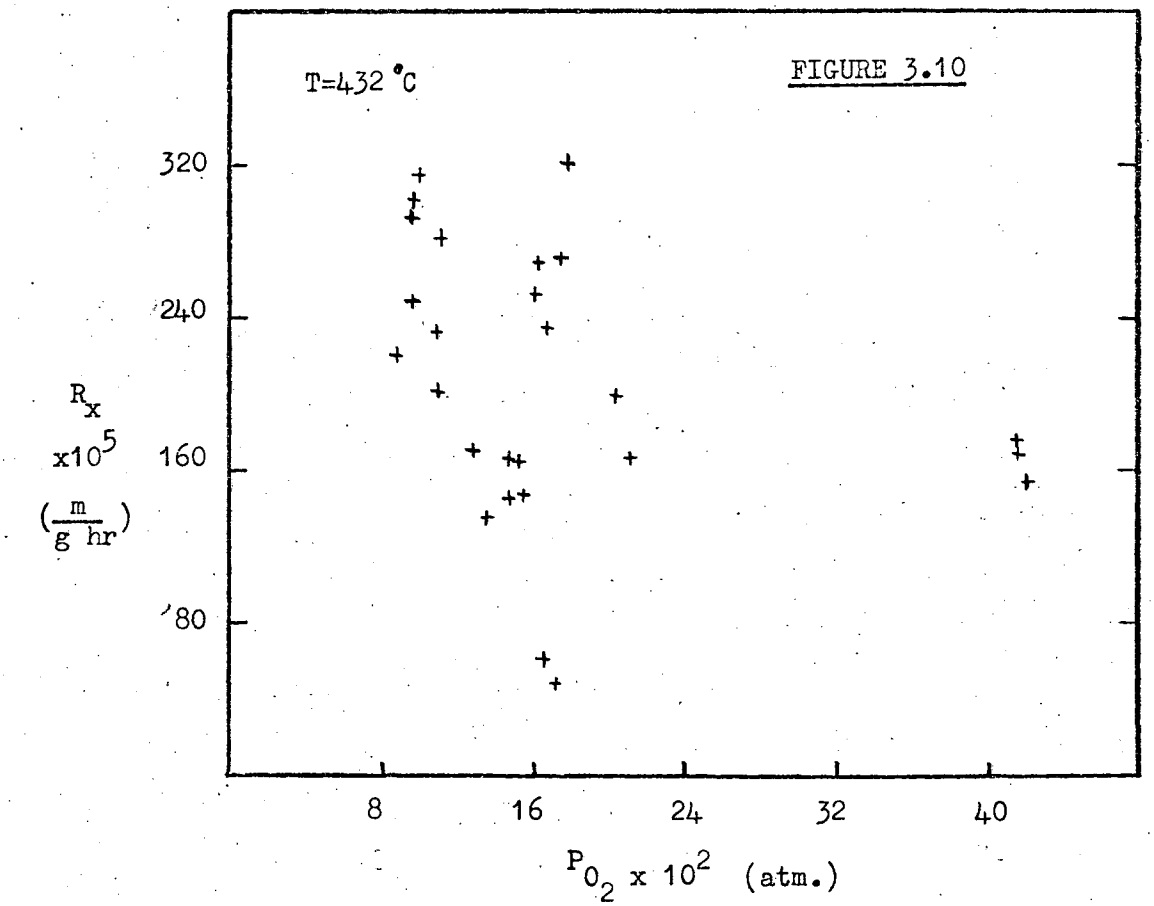


FIGURE 3.10



3.7.2 Product Formation and Selectivity

The products identified from the oxidation of o-xylene were phthalic anhydride (the main organic product), o-tolualdehyde, phthalide, and carbon dioxide. Traces of maleic anhydride and o-toluic acid were occasionally found but these were never of sufficient size to be quantified; the maleic anhydride was found mainly at 432°, but the toluic acid was not found significantly more at one temperature than at the others.

An inspection of the selectivities shows that they vary considerably at all the temperatures, but that those at 391° and 432° are generally lower than those at the two intermediate temperatures. These low selectivities at the extreme temperatures were directly responsible for curtailing the temperature range of this study to 40°, since a reasonably accurately measurable amount of phthalic anhydride was necessary to permit calculation of the xylene concentration.

Only rarely was a selectivity of greater than 50% achieved, generally they were much lower than this, averaging, for example, 25 - 30% at 432°C. This is in marked contrast to the work of Caldwell[30], who obtained yields of approximately 65% in his fixed-bed reactor, with the same catalyst and a 1% xylene feed.

Although Ross[31] had concluded from his work on naphthalene oxidation, in basically the same system as used here, that the consecutive reaction of phthalic anhydride to carbon dioxide was small, the poorer selectivities at the higher temperatures in this study suggested that significant phthalic anhydride combustion was ocurring; and so an investigation was made.

3.7.3 Homogeneous Combustion of Phthalic Anhydride

The combustion of phthalic anhydride was investigated by feeding the product stream from the aluminium block fixed-bed reactor directly to the spinning basket reactor, as described in section 2.4. This stream consisted of:

phthalic anhydride	0.43%
xylene	0.30%
oxygen	17.08%
carbon dioxide	1.90%

(the remainder was mainly nitrogen)

The assumption was made that the carbon dioxide formed in the spinning basket reactor came only from phthalic anhydride, and, on that basis, the percentage of the inlet phthalic anhydride that had combusted was calculated.

The results of the runs performed without catalysts are presented in Figure 3.11. Two runs with catalyst present gave marginally increased combustion, but this is most probably due to the oxidation of some of the inlet xylene.

The accuracy of these results is much poorer than normal for the following reasons:

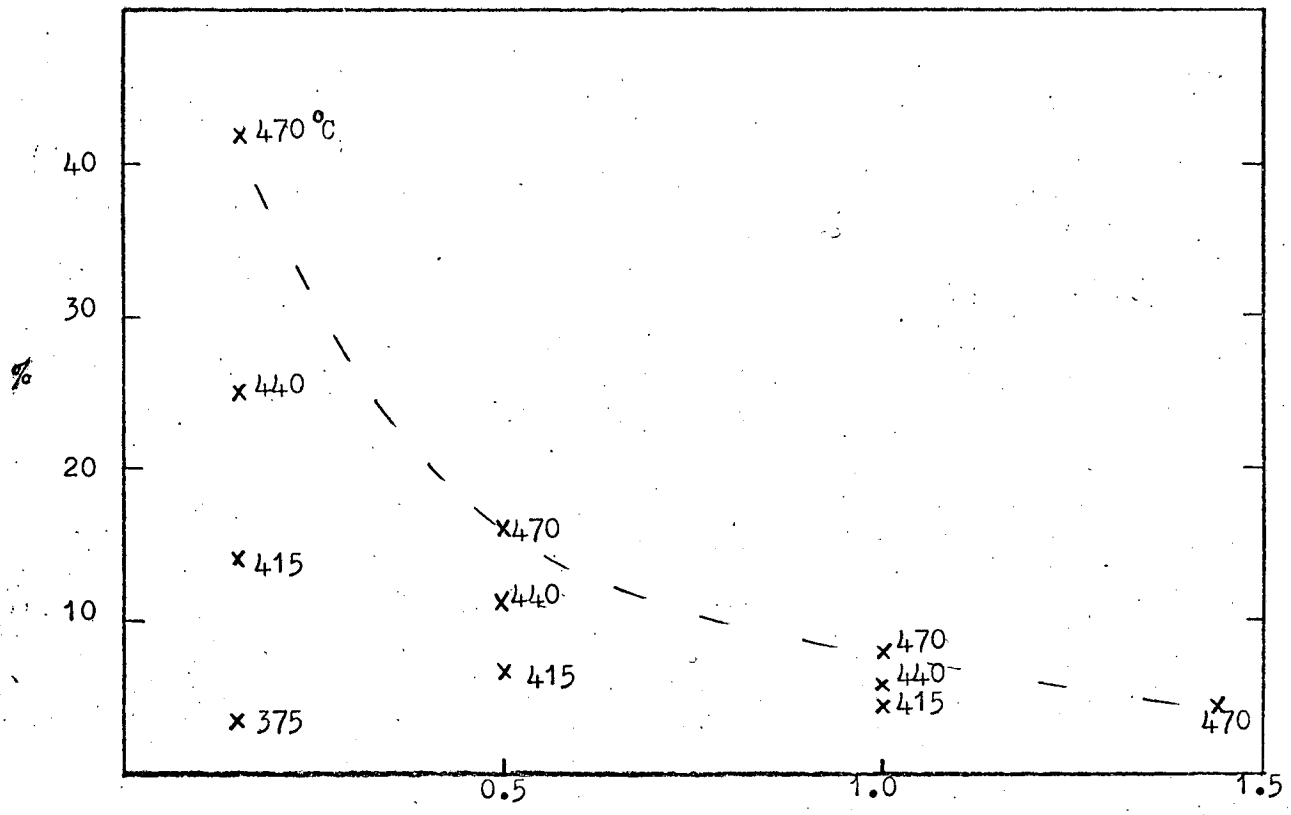
a) the experimental system employed was very difficult to control. Slight changes in the pressure at the fixed-bed collection system caused major disturbances to the flow to the C.S.T.R. along the linking pipe.

b) the flowrate was metered as air after the C.S.T.R.

c) imperfect mixing was obtained at the higher flows.

FIGURE 3.11 - PHTHALIC ANHYDRIDE HOMOGENEOUS COMBUSTION.

Fraction of inlet P.A. to the C.S.T.R. which combusts versus Flowrate.



Flowrate - litres/min at N.T.P.

d) at the higher flows, the electrostatic precipitator could not collect all the exit phthalic anhydride, and so the exit carbon dioxide was the only reading taken.

Nevertheless, these results clearly show that significant homogeneous combustion of phthalic anhydride can occur over the whole temperature range at the conditions used in this study.

Ross studied naphthalene oxidation at temperatures of 331°, 353°, 380° and 422°C, and at flowrates generally lower than used in this study; he observed a maximum selectivity to phthalic anhydride between 353 and 380°. His conclusion that phthalic anhydride combustion was small was based on the fact that, over his whole range of operating conditions, he obtained a correlation between the rate of naphthalene disappearance and the rate of phthalic anhydride appearance.

Now, as Ross increased the napthalene fed to his system, he would usually thereby increase the outlet naphthalene concentration and the rate of napthalene disappearance. Except for the shaft purge, his total flow passed through the bubbler. As he worked at a constant bubbler temperature, he would increase the inlet naphthalene and hence its rate of disappearance, by increasing the total flow through the reactor. The consequent decrease in residence time would cause a decrease in the phthalic anhydride homogeneous combustion. And so, his increase in naphthalene disappearance rate would also result in an increase in phthalic anhydride appearance, and hence the correlation.

It is believed, therefore, that significant homogeneous combustion of phthalic anhydride also occurred in Ross's experiments.

3.7.4 Effect of Fixed-Bed Tail Gas and Carbon Dioxide Addition

Bernardini et al[32], as already mentioned, studied the oxidation of pure phthalic anhydride in the same fixed-bed reactor system that they used for o-xylene oxidation. They found the level of combustion so large that they could explain their high yields of phthalic anhydride from o-xylene only by postulating phthalic anhydride combustion inhibition in the latter case.

It was decided to feed the tail gas from the fixed-bed reactor to the C.S.T.R., to see whether it caused any combustion inhibition.

Four of the kinetic runs at 432^{o} were repeated with tail gas being substituted for the bubbler bypass stream. No account was taken in the mass balance of any xylene entering in the tail gas. If it is assumed that no xylene was collected on the layers of phthalic crystals or on the tightly packed glass wool in the fixed-bed collection system, then the maximum xylene concentration of the tail gas was 0.3%. As the xylene input stream (2 - 2.5% xylene) was always greater than this tail gas stream, the input xylene error was less than 10%. The selectivity in the four kinetic runs was approximately 30% and one would not expect the xylene in the tail gas to be subject to a significantly different value. Therefore the xylene in the tail gas should not increase the phthalic anhydride formed by more than 3 - 4%.

The four runs were then repeated again with, this time, the carbon dioxide removed from the tail gas.

The results are presented fully in Appendix 2, but a summary is presented in Table 3.1.

Table 3.1

Effect of Tail Gas and Carbon Dioxide Addition

Run	Conversion	Yield	Concentration of Xylene	Concentration of Oxygen	R_X	R_{PA}	Concentration of CO_2
	%	%	%	%	(m/ghr x10^5)		%
73 S	50.8	16.0	0.64	16.2	256	81	-
74 A	51.4	12.9	0.60	14.7	242	61	-
75 B	49.5	16.9	0.68	15.6	246	84	-
79 S	68.5	23.4	0.64	17.4	268	91	-
80 A	67.4	18.3	0.68	14.6	271	74	-
81 B	68.6	27.0	0.64	16.6	261	103	-
82 S	73.7	22.5	0.51	9.8	248	75	-
83 A	73.7	19.5	0.54	6.9	259	68	-
84 B	71.4	22.6	0.56	8.7	241	76	-
85 S	69.3	25.1	0.70	17.9	320	116	-
86 A	71.0	22.7	0.64	16.4	322	103	-
87 B	68.9	26.2	0.75	16.9	337	128	-
67 S	74.0	13.0	0.22	15.8	146	26	3.6
70 C	89.9	8.5	0.14	9.5	159	15	7.3
68 S	65.5	9.8	0.31	42.9	153	21	2.2
71 C	80.9	5.4	0.30	35.5	189	13	7.4

S Standard Run

A Tail Gas with CO_2

B Tail Gas without CO_2

C Carbon Dioxide Addition

Surprisingly, the CO_2 - containing tail gas caused a reduction in the measured phthalic anhydride appearance rate of as much as 15%.

When the carbon dioxide was removed from the tail gas, by the use of a sodium hydroxide bubbler, the phthalic anhydride appearance rate was restored to the original value or increased above it.

Two runs were performed with the direct addition of carbon dioxide to the inlet; they are included in Table 3.1 and compared with the two nearest standard runs. Although these two standard runs were performed with a different weight of catalyst, they have outlet conditions similar to those of the CO_2 addition runs.

Again the rate of phthalic anhydride appearance is considerably smaller in the runs with the high carbon dioxide concentration.

Little information can be gained about this phenomenon from the standard runs, since a high selectivity to phthalic anhydride immediately implies a low level of combustion.

Although the evidence for combustion inhibition by CO_2-free tail gas is inconclusive, clearly the addition of carbon dioxide to the system is detrimental to the production of phthalic anhydride.

3.7.3 Catalyst Ageing and Colour Effects

After the initial few hours of operation, no change in the catalyst activity was apparent in batches used for over 100 hours.

The catalyst colour could only be inspected, of course, after the reactor had been cooled from reaction temperature and opened. As the catalyst aged, there was a general change of the colour from yellowish to black.

The only occasion when a change of black to yellow was observed was after a series of runs in which tail gas had been added.

The only constant feature of the catalyst colour was that all the pellets always had the same colour after a run, even when the run had begun with mixed yellow and black pellets.

3.7.6. Restriction of Data Interpretation

The investigation of the homogeneous oxidation of phthalic anhydride showed that the extent of oxidation, although considerable, was not itself sufficient to explain the drop in selectivity from Caldwell's value of (approximately) 65%. The selectivity to organic products was less than 20% at temperatures below 390°C; in contrast to the low temperature (290 - 310°C) work of Juusola et al[41], no high selectivities to tolualdehyde were obtained. In view of the ease of homogeneous oxidation of tolualdehyde at room temperature and of the long residence times in the C.S.T.R., it is probable that tolualdehyde also was being homogeneously consumed.

The existence of these homogeneous reactions, together with the catalytic formation of phthalic anhydride (via intermediates), the probable xylene catalytic combustion, and the reactions of the intermediates, results in a relatively high number of disposable parameters, a number too great to permit their determination from the limited amount of experimental data available. Consequently, quantitative consideration of the data has been restricted to the rate of xylene disappearance only.

Chapter 4

Discussion of the Spinning Basket Reactor Results

The experimental data have to be fitted to any proposed model as a whole, since it was not possible to vary systematically the xylene and oxygen concentrations. While rates were measured at a satisfactory range of xylene concentrations, the same was not true for the oxygen concentrations. The actual variation of the oxygen concentrations, presented in Table 4.1, should be borne in mind in the subsequent discussion.

Table 4.1

Variation of the Oxygen Concentrations

Oxygen Concentrations	T = 391 °C	399°C	411°C	432°C
< 5%	0 runs	0	0	0
5 - 10	0	0	3	3
10 - 15	3	4	8	4
15 - 20	12	12	12	9
20 - 25	1	0	1	2
25 - 30	1	4	1	0
30 - 35	0	0	1	0
> 35%	0	0	0	3
Total	17	20	26	21

A total of 84 runs has been used to determine the kinetic parameters; these do not include the seventeen runs mentioned in section 3.7.1 (which are discussed later) or runs with the addition of tail gas or carbon dioxide.

The xylene outlet (reactor) concentration was varied in the range 0.1 - 1.9% and the xylene conversion from 20 - 75%.

4.1 Kinetics of Xylene Disappearance - Power Law

The first equation investigated as a possible representation of the experimental data was a power law with two concentration terms:

$$R_X = k\, C_o^{\,a}\, C_X^{\,b} \qquad (4.1)$$

The advantage of this equation lies in the fact that the exponents "a" and "b" are direct measures of the relative influence of oxygen and xylene concentrations on the rate of reaction.

To determine the values of k, a and b, a linear least squares analysis was performed. The equation was first transformed into a linear form by taking logarithms:

$$\ln R_X = \ln K + a \ln C_o + b \ln C_X \qquad (4.2)$$

The logarithmic transformation equalises the weight of all the values in the least squares analysis, and so should not alter the error distribution significantly from that of the untransformed equation.

Since the oxygen concentration had not been uniformly varied, four least squares analyses were performed at each temperature, with the imposed values of the parameters given in Table 4.2.

Table 4.2

Imposed Parameter Values

Least Squares Analysis No.	1	2	3	4
k	-	-	-	-
a	-	0	1	0
b	-	-	-	1

The fit to each equation was measured by the magnitude of an error term, defined as the sum of the differences squared between the observed and calculated rates: i.e.

$$\Sigma E^2 = (R_X - R_{calc})^2 \qquad (4.3)$$

The results of the analyses are given in Table 4.3.

Table 4.3

Parameters for Equation 4.1

L-S Analysis No.	1	2	3	4
T = 391°C				
k	0.019	0.76	287.2	7.597
a	-0.62	0	1	0
b	0.745	0.760	0.784	1
ΣE^2	1.73×10^{-7}	1.98×10^{-7}	4.63×10^{-7}	2.25×10^{-7}
T = 399°C				
k	5.17	4.12	889	8.964
a	0.042	0	1	0
b	0.914	0.915	0.88	1
ΣE^2	5.48×10^{-7}	5.48×10^{-7}	1.90×10^{-6}	5.61×10^{-7}
T = 411°C				
k	22.10	6.14	6360	13.15
a	0.184	0	1	0
b	0.94	0.92	1.03	1
ΣE^2	9.59×10^{-7}	1.03×10^{-6}	7.33×10^{-6}	1.20×10^{-6}
T = 432°C				
k	10.79	12.10	23300	25.15
a	-0.015	0	1	0
b	0.92	0.92	1.10	1
ΣE^2	1.047×10^{-6}	1.06×10^{-6}	2.57×10^{-5}	1.14×10^{-6}

The equations tested were:

$$R_X = k\, C_o^{\,a}\, C_X^{\,b} \qquad (4.1)$$

$$R_X = k\, C_X^{\,b} \qquad (4.1b)$$

$$R_X = k\, C_o C_X^{\,b} \qquad (4.1c)$$

$$R_X = k\, C_X \qquad (4.1d)$$

The units of k are $(m^{1-a-b}\ \ell^{a+b}/g.hr)$.

The first equation (4.1), with no imposed parameter values, suggests an oxygen dependency of -0.6 and 0.18 at 391° and 411° respectively, and a virtually zero dependency at the other two temperatures.

More credence must be given to the two zero values, since a least squares analysis should produce a result of zero dependency only if the true dependency is zero and if the concentration in question has been varied sufficiently widely to permit its determination; whereas, irrespective of the true dependency, if the concentration was not varied widely, the analysis will produce a numerical dependency of no physical significance.

An inspection of Table 4.1 shows that, at 391°, the oxygen concentration was seldom varied outside the range 15 - 20%, and so may be assigned a virtually constant value. It is suggested, therefore, that the oxygen dependency determined at 391° is of little significance, and similarly, to a lesser extent, at 411°C.

As can be seen in Table 4.3, the imposition of a zero oxygen dependency on the analysis at all temperatures did not produce a fit which was significantly worse. The squared error term was increased by a maximum of only 12%.

With the exception of the results at 391°C, the imposition of zero oxygen and first order xylene dependencies increased the squared error by only 8%.

However, the imposition of first order dependencies on both concentrations increased this term by three - twenty-five fold, and thus this dependency can be ruled out.

Therefore, three of the tested equations (4.1, 4.1b, 4.1d) adequately represent the data; of these, equation (4.1d) has the largest squared error term corresponding to the following average errors - at 391°C, 20%; at 399°C, 15%; at 411°C, 14%; at 432°C, 11%.

The calculated parameters of equations (4.1) and (4.1b) do not provide meaningful correlations with temperature; it should be noted, however, that the 'k' values of equation (4.1b) at the three higher temperatures do.

All four of the 'k' values from equation (4.1d) satisfy a normal Arrhenius plot.

The temperature dependency of these parameters is discussed in section 4.4.

4.2 Kinetics of Xylene Disappearance - Redox Model

The kinetic equation derived from the Redox theory is:

$$R_X = \frac{k_a C_o k_X C_X}{k_a C_o + S K_X C_X} \qquad (4.4)$$

As mentioned previously, this equation is identical to the one yielded by the Steady State Adsorption Model. As this equation has been applied with success to the catalytic oxidations of several aromatic hydrocarbons, it was decided to investigate it.

An immediate problem which arises is the value of the "S" term. This term is the number of moles of oxygen consumed catalytically per mole of hydrocarbon consumed catalytically. It has already been shown that, in this study, a significant proportion of the oxygen was consumed homogeneously, and so a value of S cannot be calculated from the measured selectivities.

A value for the catalytic selectivity may be obtained from Caldwell's work since his experiments were performed at a very short residence time and may therefore be assumed free from homogeneous combustion. Based on his yields, a selectivity of 66$\frac{2}{3}$% was chosen as a reasonable value. On the assumption that the only other product is carbon dioxide, a value of 5.5 may be calculated for S.

The value was assigned to S at all the temperatures.

The parameters which gave the best fit of the data to the equation were this time calculated using an I.B.M. package[52] for nonlinear parameter estimation. In addition, a grid search technique was employed.

The results are presented in Table 4.4.

Table 4.4

Parameters for Equation (4.4)

T	k_a	k_X	ΣE^2
391	112.0	7.16	1.86×10^{-7}
399	26.6	9.63	5.49×10^{-7}
411	32.8	14.81	8.75×10^{-7}
432	834.6	24.90	1.12×10^{-6}

Although the error terms compare favourably with the Power Law equations, it can be seen immediately that these values obtained for the xylene "k" parameter are very close to the values obtained from equation (4.1d) - the power law with zero oxygen and first order xylene dependencies.

When $k_a C_o \gg S K_X C_X$, then equation (4.4) reduces to a first order xylene dependency; this is what has occurred in this case. Even at the two low values of k_a, since $C_o \sim 20 C_X$, $k_a C_o$ is over ten times greater than $S K_X C_X$.

A grid search confirmed that minima occurred at these values and also showed that, when $K_a C_o \gg S K_X C_X$, the Redox model is quite insensitive to changes in k_a, and thus will give a poor estimate of its value. This insensitivity is demonstrated in Table 4.5.

Table 4.5

Some Grid Search Results

T	k_a	k_X	E^2
391	50	7.0	1.95×10^{-7}
	100	7.0	1.89×10^{-7}
	200	7.0	1.87×10^{-7}

Because of the nature of the apparent temperature dependency of the calculated k_a values, and because the model, containing oxygen terms, effectively gives results that are oxygen independent, then this model cannot be considered satisfactory.

4.3 The Hughes-Adams Model

The rate data were also tried in the expression proposed by Hughes and Adams[29] for surface reactions in which the rate-controlling step is either the adsorption of the organic reactant or the desorption of the oxidation products. The equation is:

$$R_X = \frac{Ap_X}{1 + Bp_X} \qquad (4.5)$$

where p_X is the xylene partial pressure, in atmospheres.

The I.B.M. non-linear parameter estimation was again employed in this calculation. The results are shown in Table 4.6.

Table 4.6

Hughes-Adams Model Parameters

T	A	B	A/B x 10^3	ΣE^2	A
°C	m/g.hr.atm	$atm.^{-1}$	m/g.hr.		ℓ/g.hr.
391	0.145	18.52	7.84	1.80 x 10^{-7}	7.90
399	0.185	20.42	9.08	5.45 x 10^{-7}	10.20
411	0.263	16.46	15.95	9.97 x 10^{-7}	14.76
432	0.467	16.48	28.34	1.08 x 10^{-6}	27.01

Again, the error terms compare favourably with those from the Power Law equations.

The magnitude of B is approximately 20 atm^{-1}, and as the xylene concentration is usually less than 1%, the denominator of equation (4.5) will not exceed 1.2; this equation will therefore have an approximately first order dependency.

The closeness of the values of A (in ℓ/g.hr) to k_X from equation (4.1d) confirms this.

The parameters of equation (4.5) are capable of a reasonable Arrhenius correlation; their temperature dependencies and the thermodynamic quantities which may be derived from them are discussed in later sections.

The Hughes-Adams model, like the zero order oxygen power laws, does provide a satisfactory correlation of the data.

4.4 Temperature Dependance of the Rate Constants

4.4.1 Power Law Rate Constants

The Arrhenius plots of $\ln k$ versus $1/T$ for the k values obtained from equations (4.1b) and (4.1d) are presented in Figure 4.1.

Equation (4.1b), $R_X = k C_X^b$, yields a "b" parameter of almost constant value at the three higher temperatures (-viz. 0.92), but a value of only 0.76 at 391°C. The k values have therefore been correlated only from 399 - 432°C.

In the case of equation (4.1d), $R_X = kC_X$, the k values have been correlated over the four temperatures and also, since the imposed first order xylene concentration causes the largest increase in error at 391°C, over the three higher temperatures.

The values of k were correlated against temperature by performing a least squares analysis on the equation:

$$\ln k = \frac{-E}{RT} + \ln k_o \qquad (4.6)$$

The results are presented in Table 4.7.

Table 4.7

Power Law Parameter Temperature Dependency

Rate Equation	No. of Temps.	E(k cal/mole)	ℓnK_o	Units of k
$R_X = kC_X^{0.92}$	3	30.6	24.44	$m^{0.08}\ell^{0.92}$/g.hr.
		29.3	19.42	m/g.hr.atm$^{0.92}$
$R_X = kC_X$	3	29.3	24.25	ℓ/g.hr.
		28.0	19.20	m/g.hr.atm.
$R_X = kC_X$	4	27.6	22.99	ℓ/g.hr.
		26.3	17.95	m/g.hr.atm.

As can be seen from Figure 4.1, all three correlations fit the results well. The overall fit of the data to the four temperature first-order xylene correlation is presented in Figure 4.3.

4.4.2 Hughes-Adams Rate Constants

The Arrhenius plots of A,B, and A/B are presented in Figure 4.2. These three parameters were correlated against temperature using a least squares analysis on the equation:

$$\ell n\ (A) = \frac{-E}{RT} + \text{constant} \qquad (4.6b)$$

The results of this are given in Table 4.8.

FIGURE 4.1 - ARRHENIUS PLOT

Temperature Dependency of Rate Constants derived from the Power Law Correlations

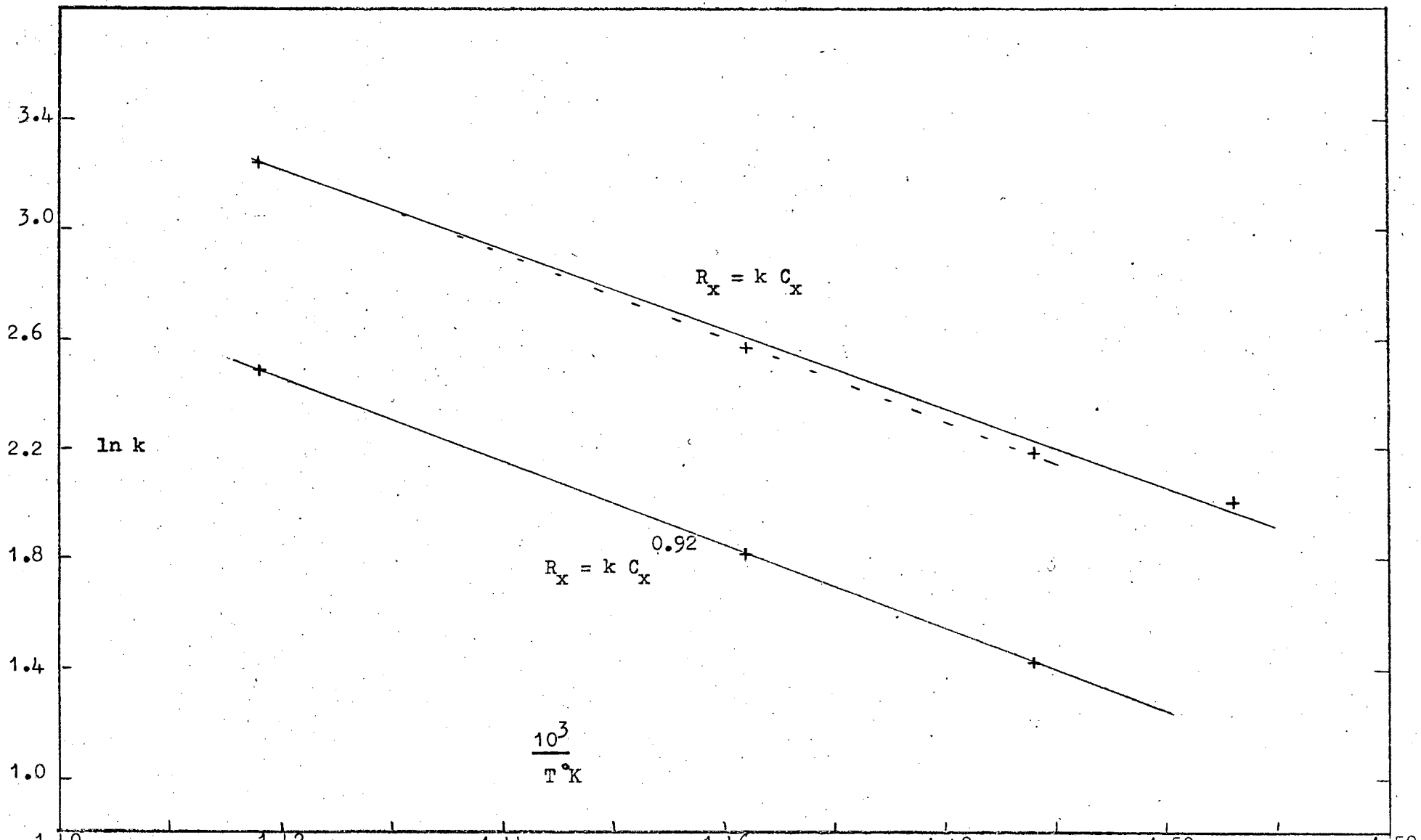


FIGURE 4.2 - ARRHENIUS PLOT

Temperature Dependency of Rate Constants derived from Hughes-Adams Equation

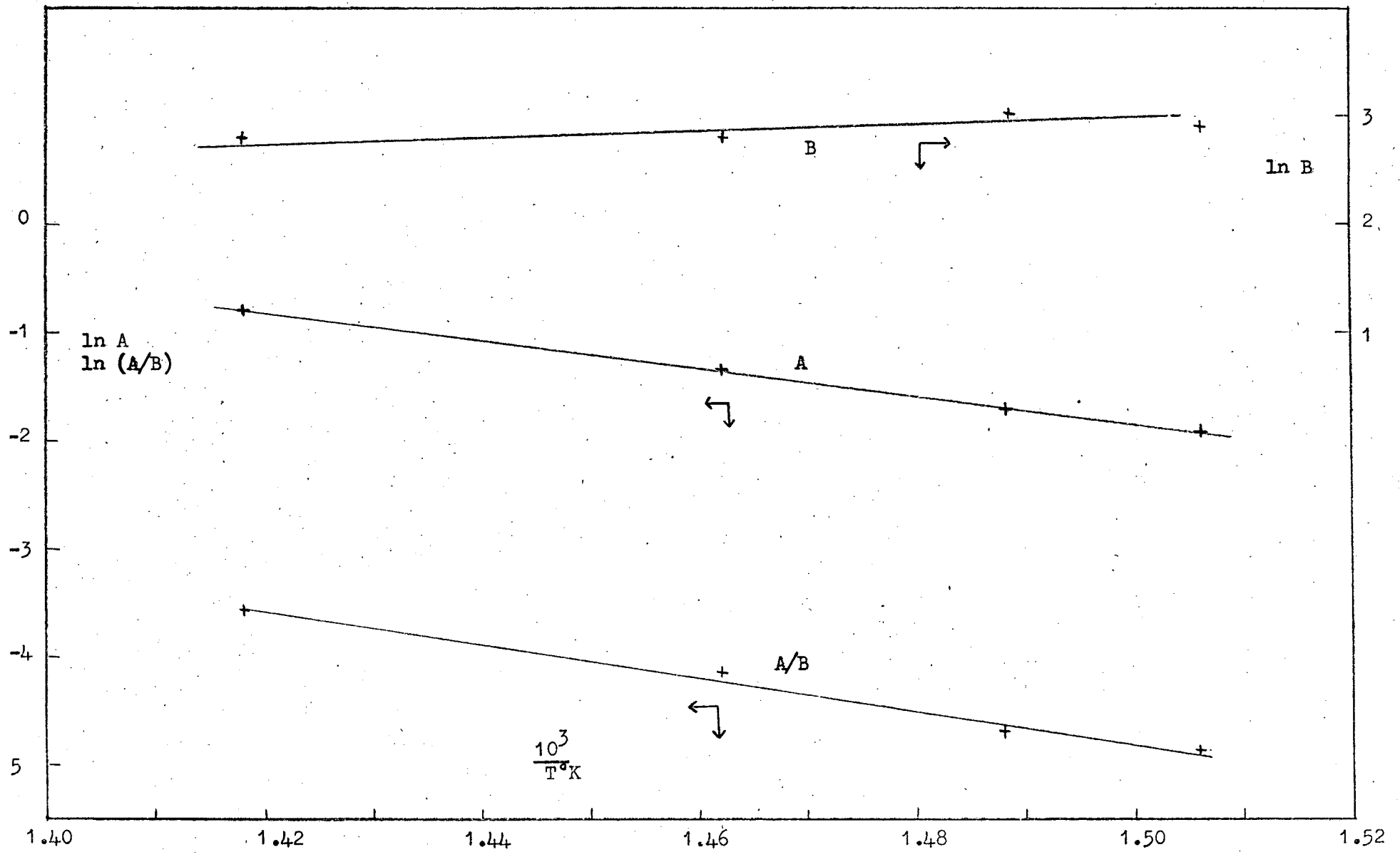


FIGURE 4.3

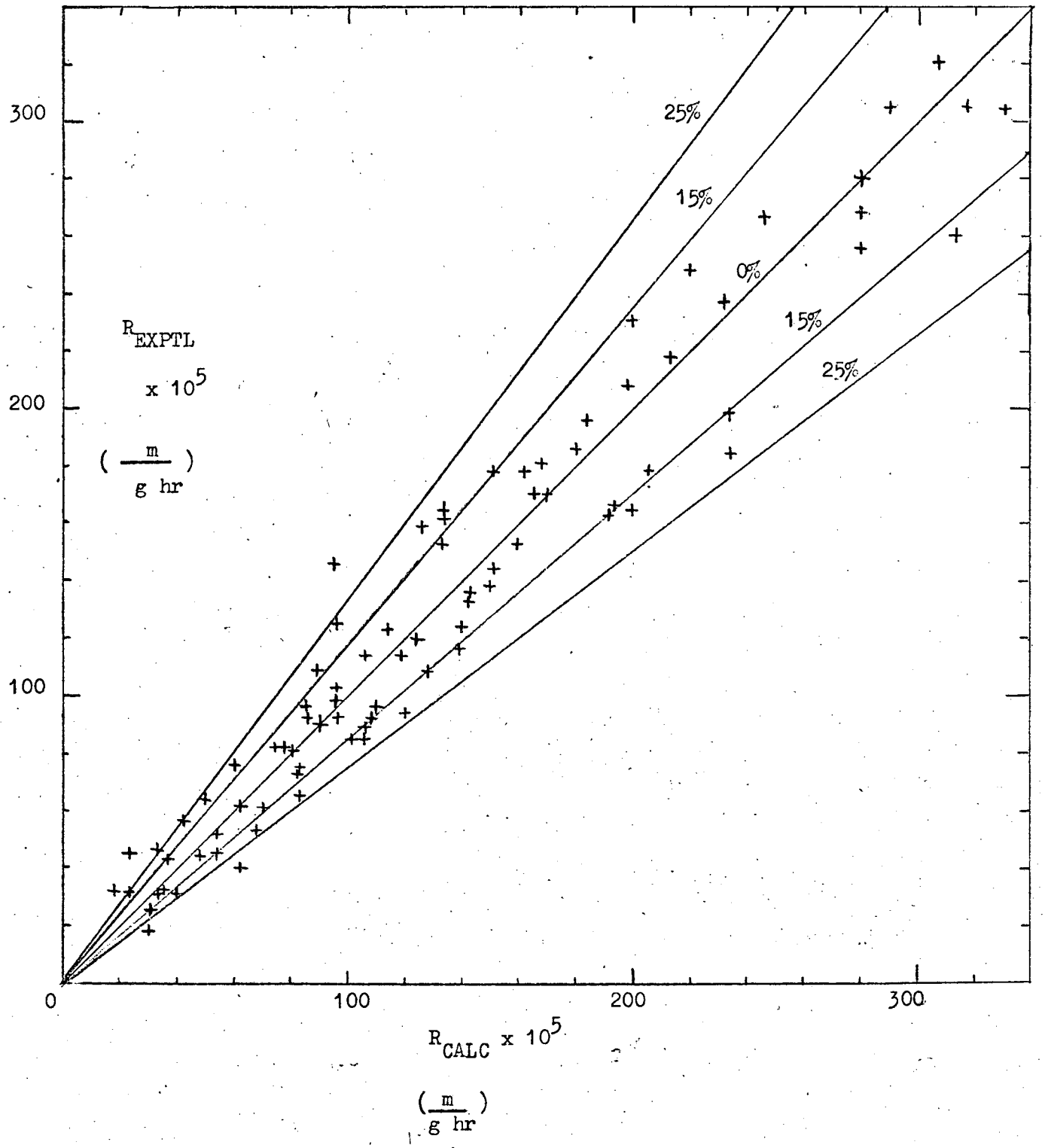

300
200
100
0
100
200
300
25%
15%
0%
15%
25%
R_{EXPTL} x 10^5
$\left(\frac{m}{g\ hr}\right)$
R_{CALC} x 10^5
$\left(\frac{m}{g\ hr}\right)$

Table 4.8

Hughes-Adams Parameter Temperature Dependency

Parameter	E(kcal/mole)	Constant
A	26.4	18.14
B	-3.89	-0.003
A/B	30.3	18.14

The Arrhenius plot of B gives only a moderate fit.

Two limiting cases of this model may be considered:-

(a) irreversible adsorption and (b) equilibrium adsorption.

As described in the derivation of the Hughes-Adams model in Chapter 1 the heat of activation for the irreversible adsorption of xylene (ΔH_1^*) and for the desorption of oxidised xylene (ΔH_2^*) may be obtained from the slopes of the lines for A and A/B respectively.

In the case of equilibrium adsorption and assuming a slow desorption of oxidation products from the catalyst, then B = K, the adsorption equilibrium constant; the heat of adsorption of xylene (ΔH_1) may be got from the slope of the line for B. The heat of desorption (ΔH_2^*) is independent of the nature of the adsorption step.

The free energy and entropy changes may then be calculated from the conventional thermodynamic equations:

$$\Delta G = - RT\ell mK \qquad (4.7)$$

$$\Delta G = \Delta H - T\Delta S \qquad (4.8)$$

The results of these calculations and of similar ones by Hughes and Adams for phthalic anhydride and by Vrbaski[28] for o-methylbenzyl alcohol are given in Table 4.9.

Table 4.9

Thermodynamic Quantities Derived from A and B

Reactant	Irreversible Ads.		Equilibrium Ads.			
	ΔH_1*	ΔH_2*	ΔH_1	ΔH_2	ΔS_1	ΔG
o-Xylene	26	30	-3.9	30	-0.006	-3.9 at 411°C
o-M.B.A.	15	31	-16	31	-13	-8.1 at 320°C
P.A.	11	44	-33	44	-29	-9.2 at 542°C

The units of S are cal/°K mole; the units of the other terms are kcal/mole.

The heat of activation for the irreversible adsorption of xylene (ΔH_1*) is considerably greater than that for the other two compounds, and is more suggestive of a heat of reaction. It is difficult to attach significance to the similarity of the ΔH_2* terms since, in each study, the oxidised products are different.

In the case of equilibrium adsorption, the adsorption terms for xylene have much lower values than for the other two. The equilibrium adsorption constant K(=B) is also much lower for xylene than for methylbenzyl alcohol and phthalic anhydride.

However, on the basis of the calculated thermodynamic quantities, neither irreversible adsorption/nor equilibrium adsorption can be ruled out.

The strong trend towards a first-order xylene dependency which the results exhibit means that B will have a small magnitude in the Hughes-Adams equation, and thus the equation will be insensitive to changes in the value of B; the data fitting to this equation will therefore give a poor estimate of its value.

As already stated, the Arrhenius plot of B gives only a moderate fit.

It is debatable, therefore, how much reliance should be placed on the values of these thermodynamic quantities derived from B.

Because of the good fit of the data to the Hughes-Adams equation, and of the reasonable Arrhenius plots of its parameters, this equation can, nevertheless, be considered satisfactory. It should be noted that for the purpose of extrapolation to higher temperatures, since B decreases with rising temperature, this equation will tend to a first-order xylene dependency.

4.5 Mass and Heat Transfer Effects

It is important to determine whether mass and heat transfer processes have had any significant effect on the calculated kinetic parameters.

The effect of pore diffusion may be considered negligible since the catalyst was surface-coated and of low surface area; therefore only external transfer processes will be considered.

Since the experimental rates have no dependence on the oxygen concentration, obviously oxygen transfer processes may be neglected.

Measurements[53] of naphthalene transfer in a stirred reactor similar to the one used in this study give a value of $k_g = 2 \times 10^{-7}$ m/cm^2 sec. mm Hg at 3000 r.p.m. In the absence of further data, this value will be taken as an approximate value for the mass transfer process in the system. If it is assumed that the surface area of the catalyst available for mass transfer was that of a sphere of the same diameter, then a value for "a" of 4 cm^2/g may be calculated.

This then gives a value for Kga of 2.2 m/g.hr.atm. or 130 ℓ/g.hr. (at 432°C). This is considerably greater than the value for k_X of 25 ℓ/g.hr. calculated from the Power Law correlation.

On the basis of this mass transfer value, the true kinetic rate constant may be calculated from the equation:

$$k_X = \frac{(k_g a).k}{k_g a - k} \qquad (4.9)$$

where k is the experimentally-determined value. The result of this calculation gives a value of $k_X = 31$, suggesting that, at 432°C, the xylene parameter has been depressed by 20%.

However, it is believed that the effect is even less than this because of certain experiments performed at 411°C and 432°C. Two runs were performed at each of these temperatures in which, in the first, the basket rotational speed was kept at 2000 r.p.m. until the first product collection was made, and then changed to 3800 r.p.m. for the second. The speeds were changed in the reverse order in the second run. No significant difference was noticed between the two collections, although, according to the I.C.I. mass transfer data, the coefficient at 3800 r.p.m. would be virtually double that at 2000 r.p.m.

The maximum temperature difference between the catalyst and the bulk gas has been calculated using a maximum xylene disappearance rate of 0.003 m/g.hr. and a selectivity of 30% and the data given in Reference 45. This gives a maximum temperature difference of approximately 5 - 6°C on the assumptions that the heat of reaction is generated uniformly on the catalyst surface and all transfer occurs by convection.

This is probably a considerable over-estimate, since considerable heat is being generated homogeneously, and, at 432°C, radiation should be significant.

Therefore, neither heat nor mass transfer effects have significantly affected the results.

4.6 Other Kinetic Measurements

As stated in section 3.7.1 seventeen runs gave results which did not fit the general trend.

It was found during the initial investigation of the catalyst's active range that when a sample of catalyst was heated from room temperature to temperatures less than (approximately) 390°C, a catalyst of virtually zero activity resulted whereas the cooling of a sample from 430 - 450°C down to 360 - 390°C produced a catalyst of considerable activity. For this reason as already stated in Chapter 2, the reactor was normally maintained at 400°C when runs were not being performed. It is presumed that the two runs at 391°C giving very low rates were due to the catalyst being in a non-active state, since they were runs performed with catalyst which had been left at room temperature for over a week, due to a holiday period.

The nature of this non-active state is unknown but the temperatures above which the catalyst becomes fully active correspond well to the temperatures above which Clark and Berets[83] found bulk defects in the catalyst lattice to be mobile. It is of interest to note that the runs performed at 348° and 366°C (with catalyst which had been used at higher temperatures for many hours) resulted in xylene disappearance rates of less than half the values predicted by an extrapolation of the 391-432° kinetic data down to these temperatures.

The most probable cause of the apparent catalyst deactivation found in the five high-concentration (i.e. greater than 1.5% xylene) runs at 432°C and the two at 399°C is a reduction of the catalyst to a state near V_2O_4 as found by Simard et al[24]. The effect is similar to that observed by Ross[31] in his study of naphthalene oxidation. Although one of the 399°C deactivated runs was not at high concentration, it was the first run performed after the five deactivated runs at 433°C, and so strongly suggestive of a physical change in the catalyst. This change was quite reversible, as successive runs at 399°C all exhibited normal activity.

Eight of the runs performed at 411°C show the same trend as the other twenty-six, but have rates approximately 1.8 times greater than those at similar xylene concentrations. These eight runs cannot be uniquely distinguished from the other runs by any of the measured concentrations, temperatures or flowrates. All of these high-rate runs are contained in a group of twelve successive runs, the other four of which exhibited normal activity, indicating a completely reversible cause.

A possible cause of these high rates is, again, a change in the catalyst oxide state. Hughes and Adams[29] report a greatly increased rate of phthalic anhydride oxidation below oxygen partial pressures of 0.1 atm., and ascribe this to a change in their catalyst to a state similar to that observed by Ushakova et al[78] to be highly active for both naphthalene and phthalic anhydride combustion, thus resulting in poor phthalic anhydride selectivity.

While the measured selectivities in the eight "high-rate" runs are not greatly different from those of the "normal-rate"runs, the trueselectivity is obscured by the homogeneous reaction.

One of the eight runs was performed at a low oxygen partial pressure of 0.025 atm., the lowest used in the study, while the others had an oxygen partial pressure of 0.15 atm. There does seem, therefore, a possibility that the high rates were due to a change similar to that reported by Hughes and Adams.

The experimental data are not sufficient to permit the determination of the oxygen dependency of the xylene disappearance rate when the catalyst is in a state of other than normal activity.

4.7 Estimation of Errors from Calculated Formation of Carbon Monoxide

In section 3.2, the maximum expected errors in the xylene disappearance rate and in the xylene outlet concentration were calculated from the errors in the measuring equipment. As explained fully in Appendix 1 , a mass balance was used to calculate the xylene disappearance rate and concentration The xylene which reacted to organic products and carbon dioxide could be measured directly, and the amount of xylene which had to react to carbon monoxide to ensure an oxygen balance was then calculated. It was suggested in section 3.2, that, since carbon monoxide formation was likely to be negligible under the normal conditions of operation in this study, the magnitude of the carbon monoxide term necessary to ensure a mass balance could be interpreted as the system error.

Typical results of this are presented in Table 4.10, where the measured carbon dioxide and oxygen outlet concentrations have each been recalculated so as to produce zero carbon monoxide formation.

Table 4.10

Error via CO Formation

Run	R_X	% change	P_X	% change	% O_2	% CO_2	% Inlet Xylene to CO
	(m/ghr. x 10^5)		(atm)				
25	301	-	.0118	-	17.9	1.5	3.0
	270	-10%	.0123	+5%	18.2	1.5	0
	291	- 3%	.0120	+2%	17.9	1.8	0
85	320	-	.0070	-	19.0	5.9	3.0
	305	-5%	.0078	+11%	19.5	5.9	0
	315	-2%	.0073	+ 4%	19.0	6.3	0

The table shows the sensitivity of the calculated rate and concentration particularly to small errors in the oxygen outlet concentration. The magnitudes of the errors are similar to those obtained in section 3.2. It should be noted that the sign of the error in the xylene disappearance rate is opposite to the sign of the concentration error, thereby increasing the total error in the rate-concentration correlation.

4.8 Comparison of Results with Other Studies

The various activation energies for the rate of xylene disappearance reported in the literature are presented in Table 4.11.

The nature of Aliev's catalyst is not known. With the exception of this study, the other results in Table 4.11 refer to "German-type" catalysts.

The upper temperature limiteof Carra's[33] study was 460°C, a temperature normally considered above the range used for the "German"- type catalyst. He reports selectivities of 30-35% at 460°C, but 69% at 410°C, thereby confirming that he is outside the usual range.

Table 4.11

Comparison of Activation Energies

Investigator	E_A - o-xylene (kcal/mole)	E_A - oxygen (kcal/mole)
Novella et al[35 - 37]	15	
Carra et al[33]	31	
Aliev et al[34]	14-17	
Abo et al[20]	4-10	
Froment[12]	27	
Herten and Froment[38]	16	24
Mann and Downie[39]	9	23
Juusola, Mann and Downie[41]	28	26
This work	26	-

From the results presented by Abo[20], it seems clear that mass transfer effects were rate-controlling in his study. Since Juusola, Mann and Downie[41] conducted a later study using the same catalyst and very similar operating conditions as Mann and Downie[34], the later study will be considered to have the greater validity.

It can be seen from Table 4.11 that the activation energy for xylene oxidation found in this study is in agreement with the values reported by Juusola et al, Froment and Carra, although all of these workers' data refer to the "German" catalyst. Novella et al, Aliev et al and Herten and Froment all report values of approximately one-half the others' values.

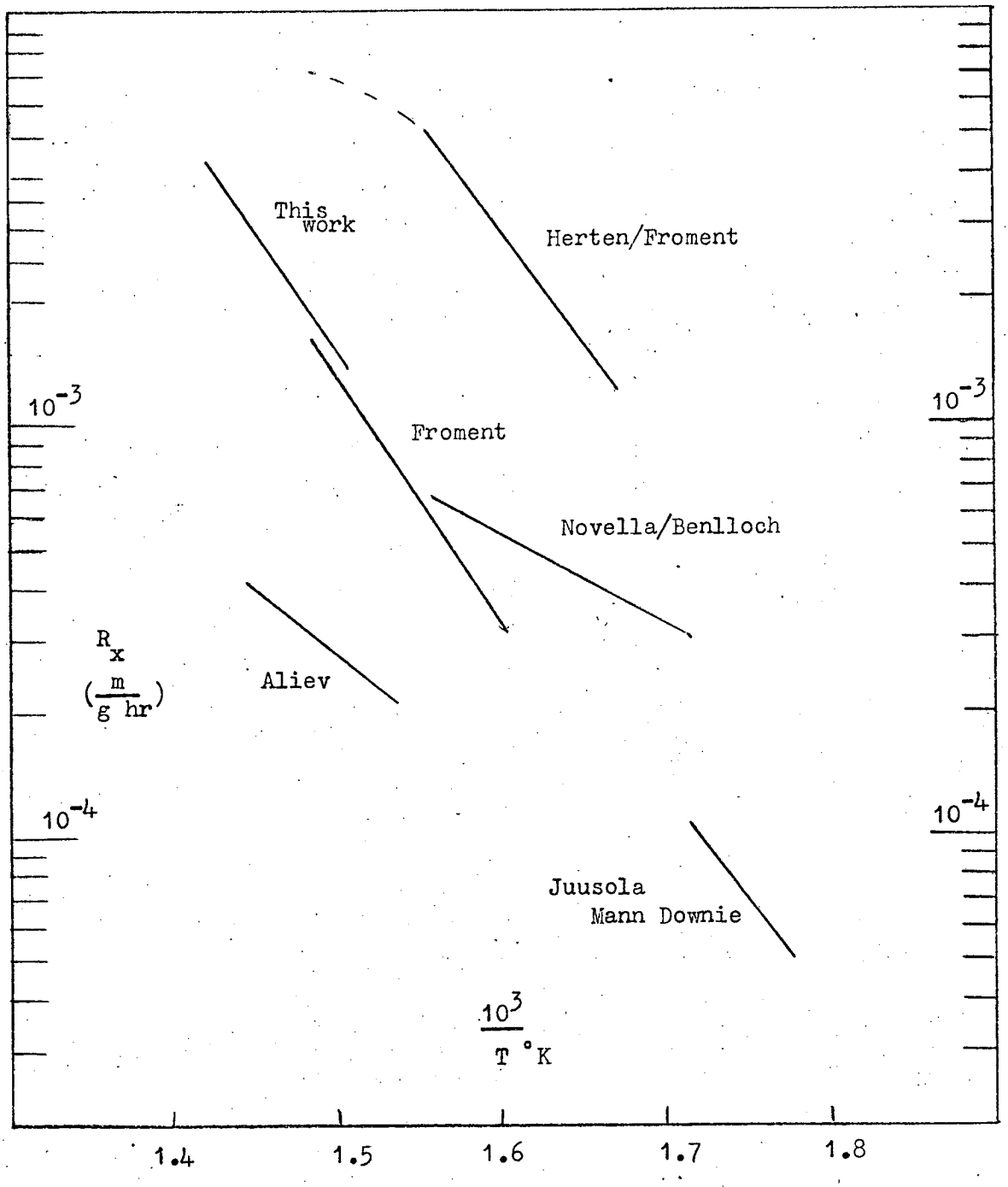
While the differences in the activation energies in Table 4.11 are no doubt in part due to the many different catalysts to which the results refer, it is interesting to speculate whether discrete reversible changes in catalyst activity (as noticed in this study) have influenced any of these results.

The activation energies for the reoxidation of the "German"-type catalyst reported by Juusola et al and Herten and Froment are in good agreement.

The independence of the rate of xylene disappearance on the oxygen partial pressure found in this study agrees with the results of Bhattacharyya and Gulati[26] who reported no difference in total conversion or product distribution in their study of o-xylene oxidation on V_2O_5 on pumice when they changed their feed stream from air to almost pure oxygen. Hughes and Adams[29] report the oxidation of phthalic anhydride on V_2O_5 on SiC to be independent of oxygen above partial pressures of 0.1 atm.

The rates of xylene disappearance reported by the various workers are shown graphically in Figure 4.4. The results of Carra et al[33] have been omitted because of the uncertainty in their absolute rates due to their mass-flow defined time base. It is apparent from Figure 4.4 that the activities of the various catalysts are all within approximately one order of magnitude.

FIGURE 4.4 - Comparison of Rates of o-Xylene Disappearance on V_2O_5 Catalysts



R_x calculated at 0.01 atm. o-Xylene and 0.21 atm. Oxygen.

The suggested continuity in Figure 4.4 of the results of this study and of those reported by Froment[12] is misleading. It is only with difficulty that any activity can be obtained from the catalyst in this study at temperatures below 380°C, and even then the activity is substantially below that expected from an extrapolation of the 391-432°C kinetic results. The rates have been calculated per unit mass of catalyst, but as Froment quotes a pellet diameter of half that used in this study, and as the "German"-type support is porous (although the V_2O_5 is believed to be in the liquid state within the pores), the rates per unit surface area would have been quite different.

However, it is concluded that the xylene disappearance rate on the "American"-type catalyst, above 390°C, is of the same order as that observed with the "German"-type.

4.9 Comparison of Results Using Other Catalysts

A total of eight runs was performed with two other catalysts (their specifications are given in Chapter 2). These runs were performed before the standard kinetic runs at conditions which were not duplicated in any of the subsequent runs with the standard catalyst. The comparison is made by the calculation of the rate of xylene disappearance over the standard catalyst, from the rate equation already derived, at the conditions of the non-standard runs. The results are presented in Table 4.12.

The full operating conditions in these runs are presented in the Appendix. Both catalysts were considerably less active than the standard catalyst. Ross[31] reports that in the case of naphthalene oxidation, catalyst 2, is several times more active than the (xylene) standard catalyst 1.

Table 4.12

Relative Rates of Xylene Disappearance

Catalyst	Temperature	Rate/Standard Rate	Selectivity
2			
(V_2O_5/SnO_2	374°C	0.10	30%
on alumina)	392°C	0.28	43%
	396°C	0.22	34%
	423°C	0.42	13%
3			
V_2O_5/K_2SO_4	353°C	0.40	13%
on silica	386°C	0.28	15%
	405°C	0.16	6%
	420°C	0112	10%

The results in Table 4.12 must however be considered with caution, since, for some of the catalyst 2 runs, the standard rate equation has been extrapolated to a xylene concentration region where it is known that the standard catalyst is deactivated. The observed maxima in the selectivities are likely to have been caused by homogeneous product combustion, and hence the values cannot be taken as representative of the true catalytic selectivities.

Chapter 5

The Fixed-Bed Reactor Results

Caldwell's[30] experiments were conducted under highly non-isothermal conditions (wall temperatures of 370-430°C, "hot-spots" of the order of 600°C) and contact times of approx. 0.3 secs., whereas the spinning catalyst-basket reactor experiments in this study were conducted under isothermal conditions (391-432°C) and contact times of the order of 5 seconds. It was decided to operate the 2 inch diameter fluid-bed reactor as a fixed-bed at conditions intermediate between Caldwell's experiments and the C.S.T.R. experiments to aid the comparison of the two sets of results.

5.1 Range of Study

A total of 32 runs was performed during which product collections were made. A further seven runs were conducted without product collection for the purpose of providing a tail gas feed to the C.S.T.R., since it was found easier to maintain constant tail gas flow when the collection condenser was not fitted. The same batch of catalyst (always diluted with alundum spheres) was used in all runs, for a total time of approx. 135 hours.

The range of variables employed was:

xylene inlet concentration	- (approx.) 0.5%, 1%.
carrier gas	- Air, 12% Ox., 39% Ox.
wall temperature	- 370-490°C.
particle Reynold's No. at 400°C	- (approx.) 5,10, 20.

5.2 The Dynamic Behaviour of the Reactor

The temperature profile of the reactor was not monitored continuously, but measured at irregular intervals during the course of a run by the moving of the axially-situated thermocouple within its steel tube. The lowest point of measurement was ½ inch above the base plate; the bed depth was approx. 4½ inches.

Temperature profiles at various time intervals during the start-up of the reactor at wall temperatures of 370°C and 390°C are presented in Figures 5.1 and 5.2. Both runs exhibit the same general features - there is a general upward movement in the temperature level of the bed, with a movement of the hot spot back towards the reactor inlet, until the final steady-state profile is achieved. The final profile is very similar in these two runs, but is reached much sooner at the higher wall temperature eg. after 22 minutes at a wall temperature of 370°C the maximum measured excess temperature was only 40°C while after 21 minutes at 390°C it was 97°C. This behaviour is in accord with the general observations of Caldwell on his one-inch diameter fixed-bed. At wall temperatures of 375-385°C he found that a virtual steady-state profile with a peak temperature not exceeding 15°C above the wall temperature was attained in 3 - 5 mimutes, and persisted for up to 90 minutes when a rapid change occurred to a sharp profile with an excess peak temperature of over 100°C. He established that a slight but definite upward movement in the bed temperature level occurred throughout this so-called 90 minute induction period. With jacket temperatures above 390°C he found no such induction period; the temperature profile moved rapidly to the attainment of

FIGURE 5.1 - TEMPERATURE PROFILES DURING REACTOR START-UP

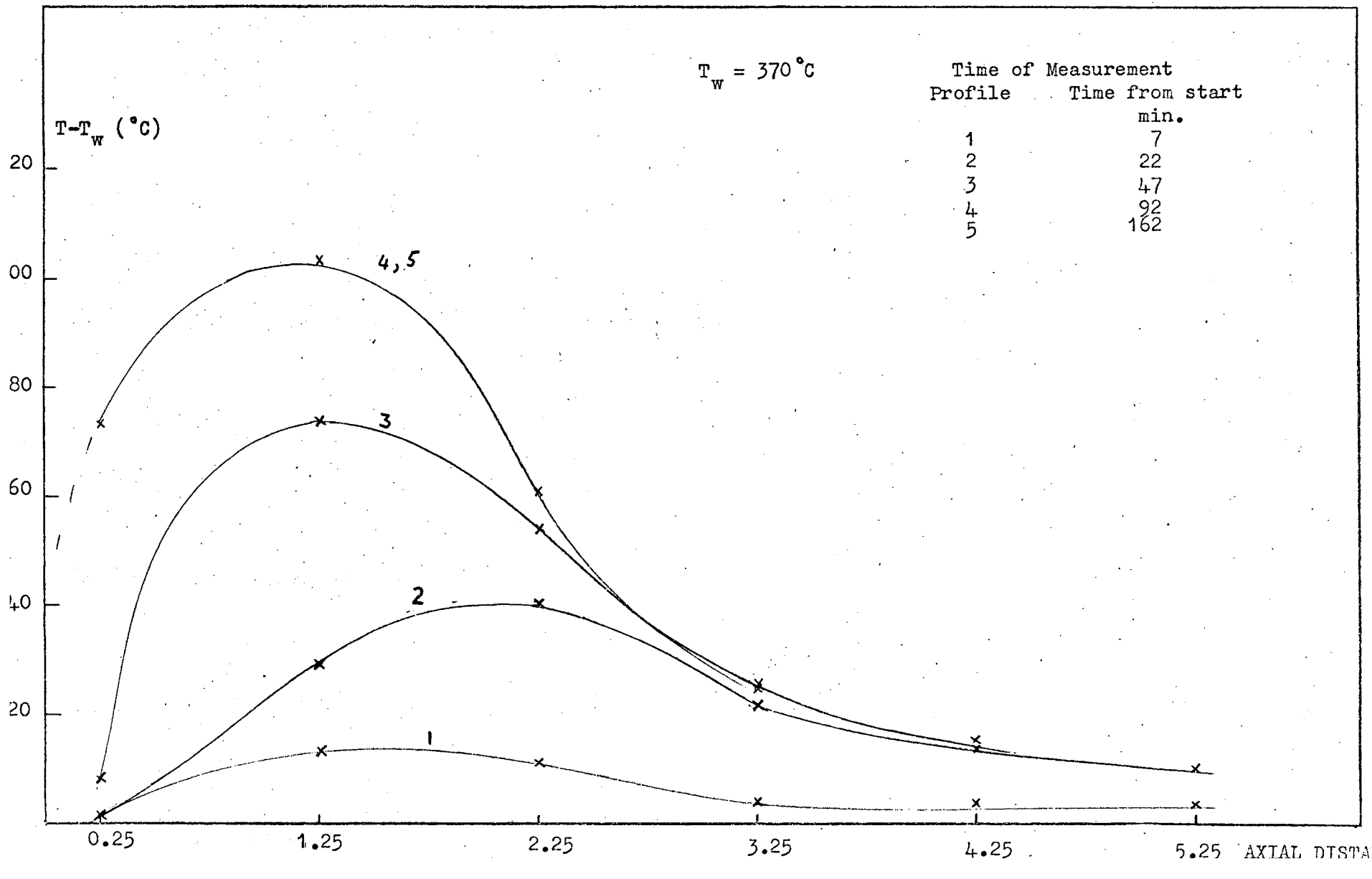
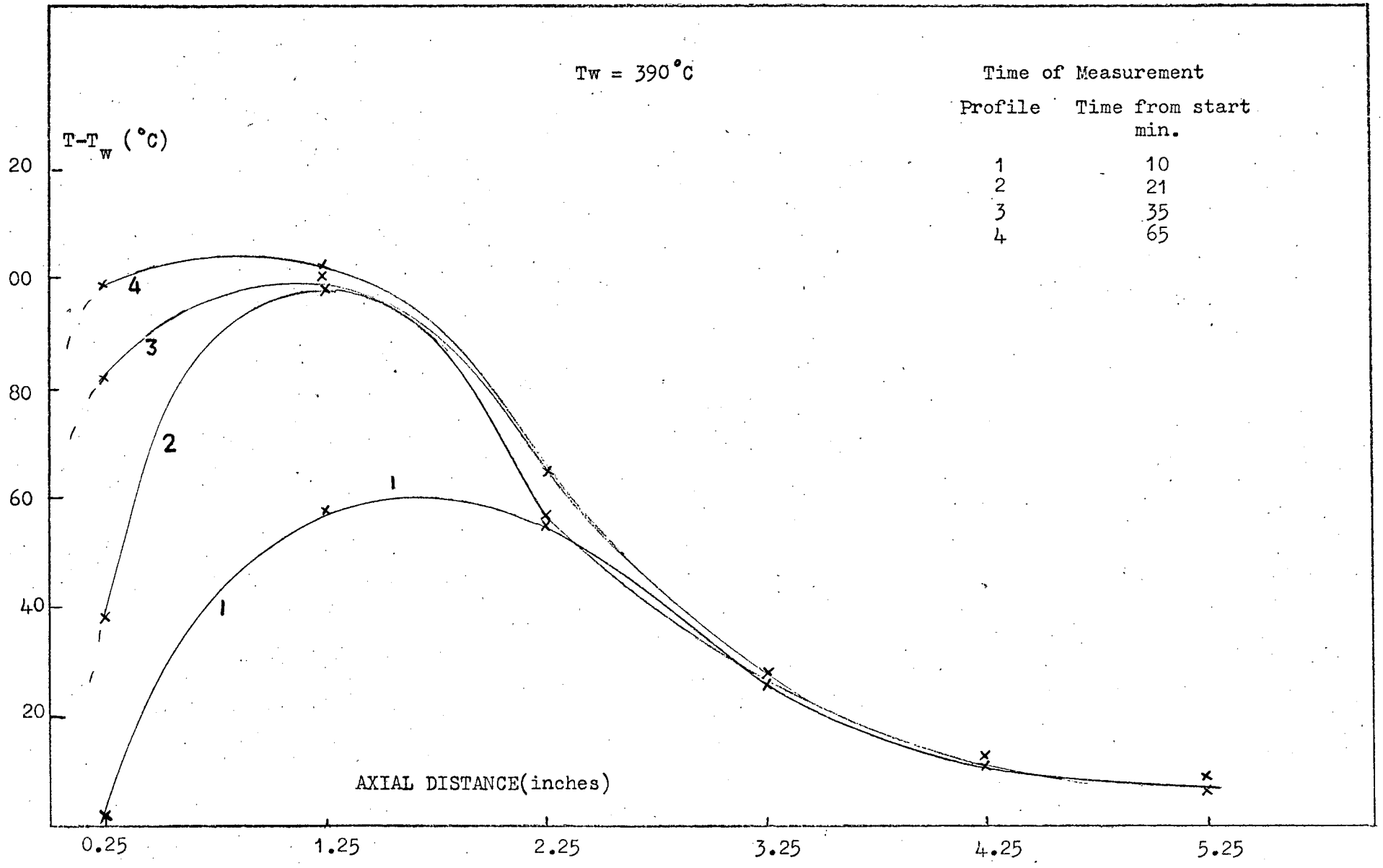


FIGURE 5.2 - TEMPERATURE PROFILES DURING REACTOR START-UP



its final high value.

Even at the lowest wall temperature of this study (viz. 370°C) no comparable pseudo-steady state induction period was observed; the movement towards the final profile was more rapid than in Caldwell's reactor. The ability to run this reactor successfully at slightly lower wall temperatures is most likely due to the poorer heat removal from this system which permits higher pellet surface temperatures for the same wall temperatures than does Caldwell's.

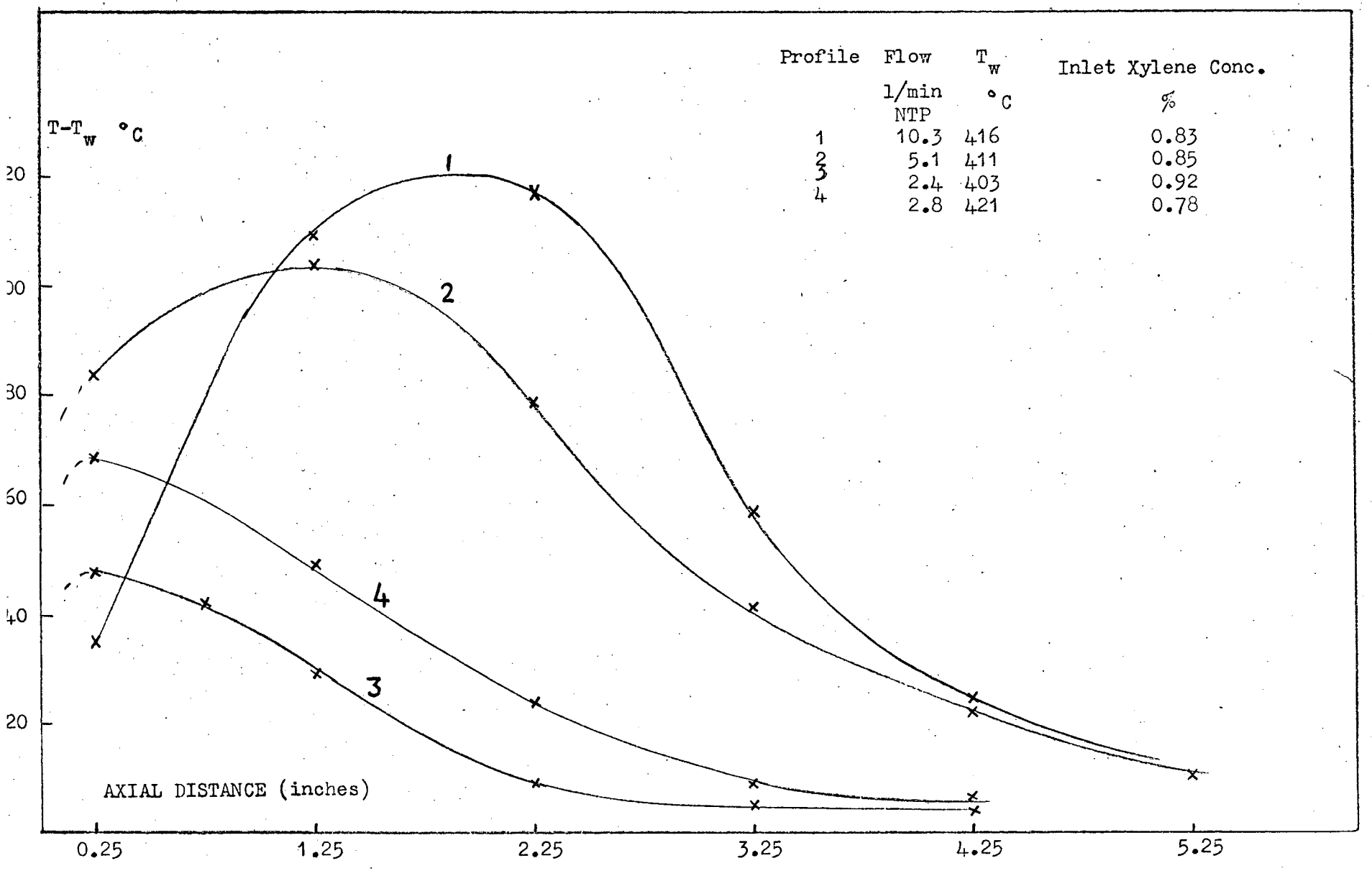
Like Caldwell, however, it was found that when the reactor was being operated with low excess temperatures (eg. immediately after start-up) low yields of phthalic anhydride were obtained and the product was discoloured; during this time the tail gas had an obnoxious smell and was of a lacrimatory nature, suggestive of only minimal oxidation of the xylene molecule.

5.3 The Steady-State Behaviour of the Reactor

Typical steady-state temperature profiles for the three flowrates normally used in the fixed-bed are presented in Figure 5.3. As the flowrate was reduced there was a decrease in the maximum bed temperature and in the bed temperature level, accompanied by a movement of the 'hot spot' towards the inlet. The lower temperatures near the inlet of profile 1 in Fig. 5.3 are most probably due to the preheater being of insufficient capacity to ensure that the feed entered the bed at wall temperature at this high flow.

Although Caldwell also found that the effect of a flow reduction was a displacement of the peak temperature towards the reactor inlet, he draws the

FIGURE 5.3 - EFFECT of FLOW on STEADY-STATE TEMPERATURE PROFILE



temperature profiles to indicate that this is accompanied by an increase in the maximum temperature. However, Caldwell's peak was normally contained within the first three feet of his seven-foot catalyst bed; his profile within this three feet was measured with three thermocouples permanently located at zero, one, and two and a half feet from the inlet respectively. He therefore admits to some uncertainty about the position and magnitude of his hot spot.

The effect of a decrease in the xylene inlet concentration is shown in Figure 5.4; it had the expected effect of a general reduction in the bed temperature level.

5.4 Conversion and Selectivity in the Fixed-Bed Reactor

The conversions and selectivities in the 32 runs are presented graphically in Figures 5.5 - 5.7 versus reactor wall temperature. At each of the three main flowrates the conversion increased rapidly above approx. 370°C and attained a virtually constant level above approx. 390°C. The conversion was never complete, this being confirmed by the collection of significant quantities of o-xylene from the tail gas in a glass wool-filled refrigerated tube. At each flow a maximum selectivity occurred at wall temperatures in the range 400 - 420°C, and the selectivity decreased significantly as the wall temperature was raised.

In spite of the much reduced temperature level at the lowest flowrate, the selectivities obtained were considerably less than at the other flows at the same wall temperature. At 460°C, for example, a selectivity of 26% was

FIGURE 5.4 - EFFECT of INLET XYLENE CONCENTRATION on STEADY-STATE TEMPERATURE PROFILE

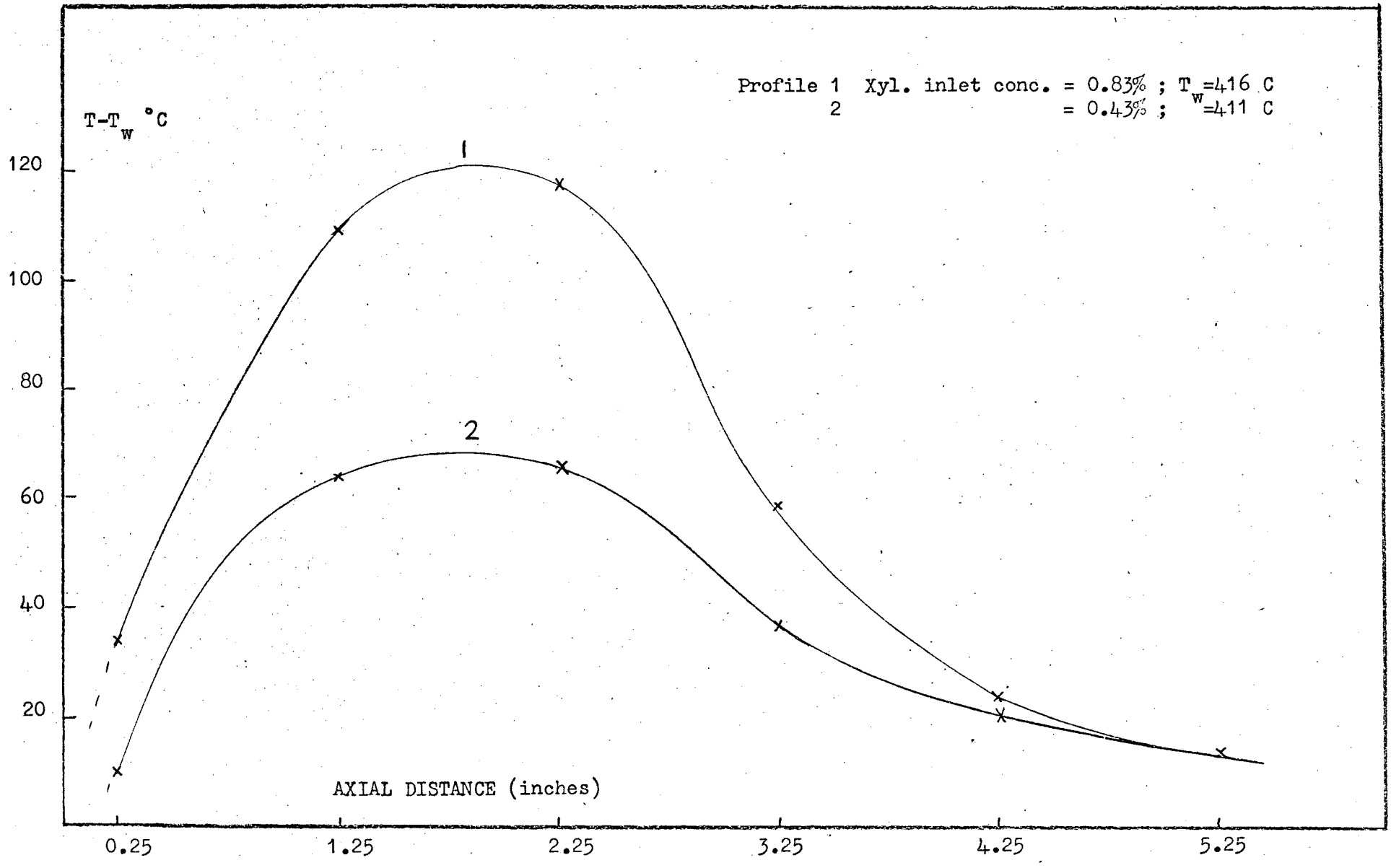
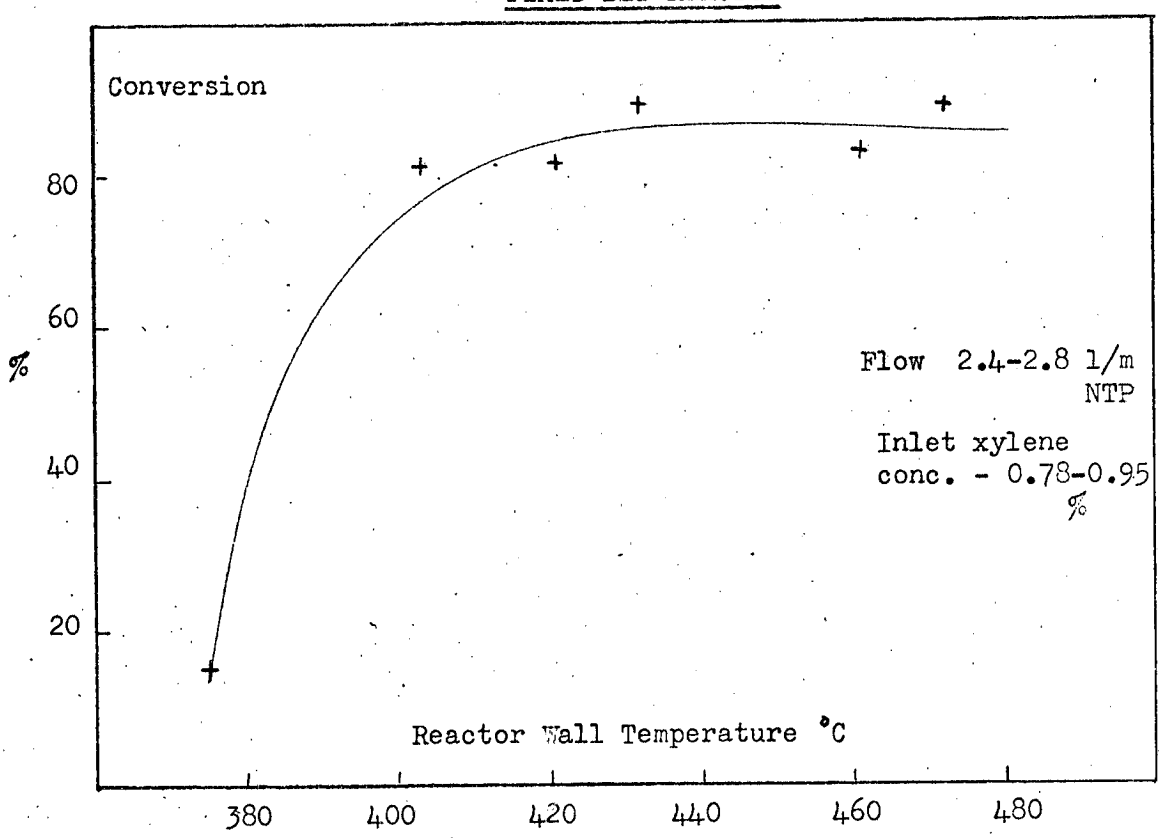


FIGURE 5.5 - CONVERSION and SELECTIVITY in the FIXED-BED REACTOR



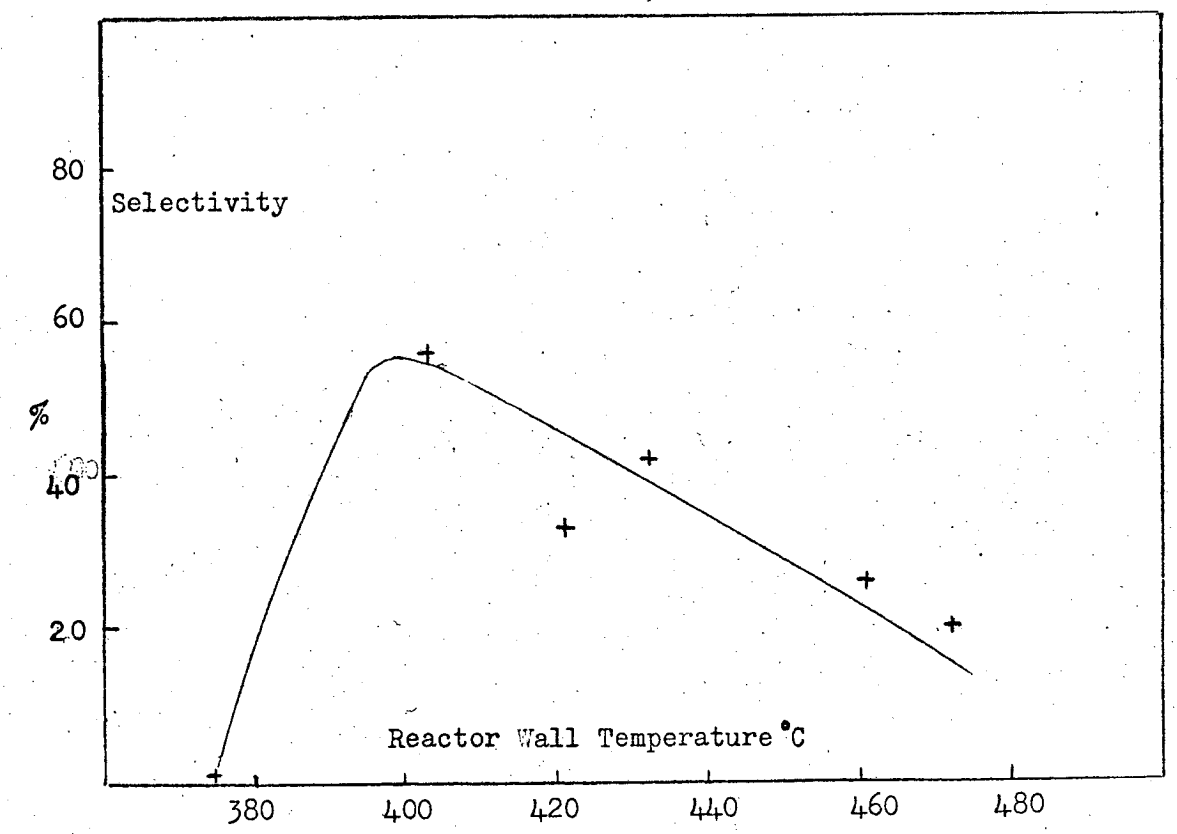
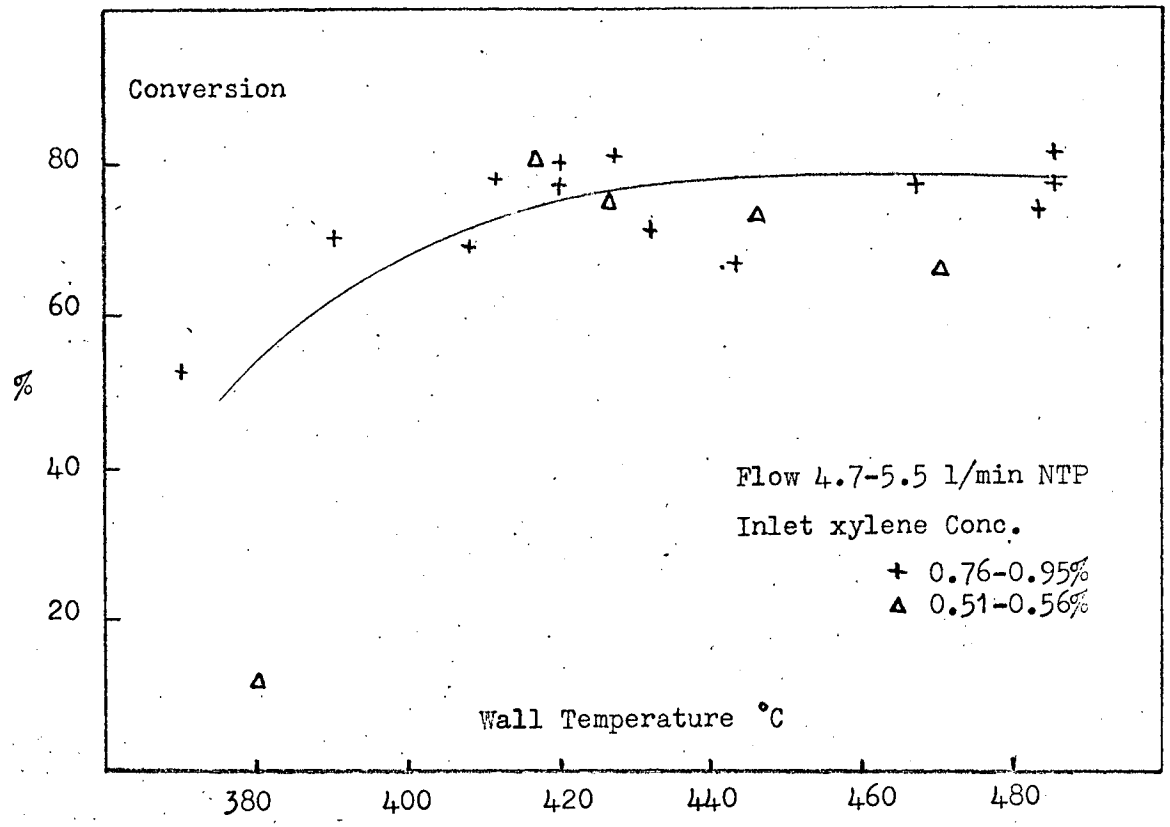


FIGURE 5.6 - CONVERSION and SELECTIVITY in the FIXED-BED REACTOR



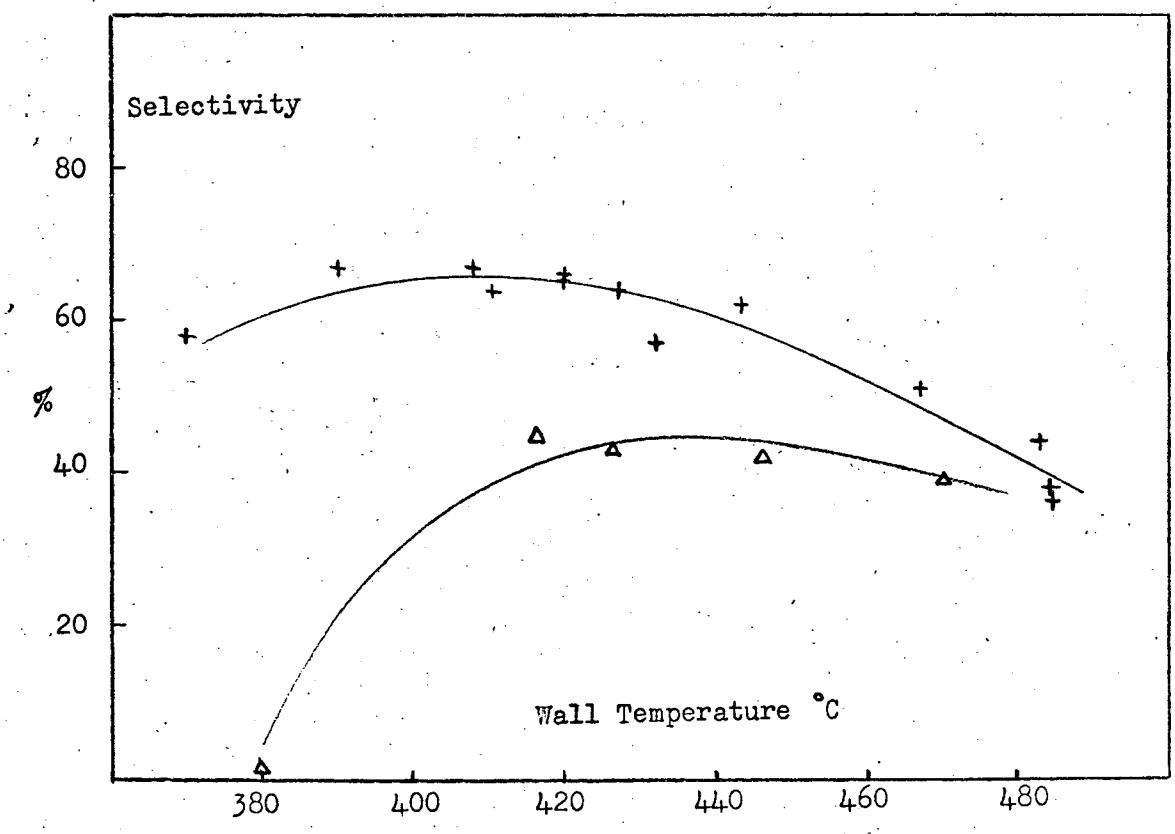
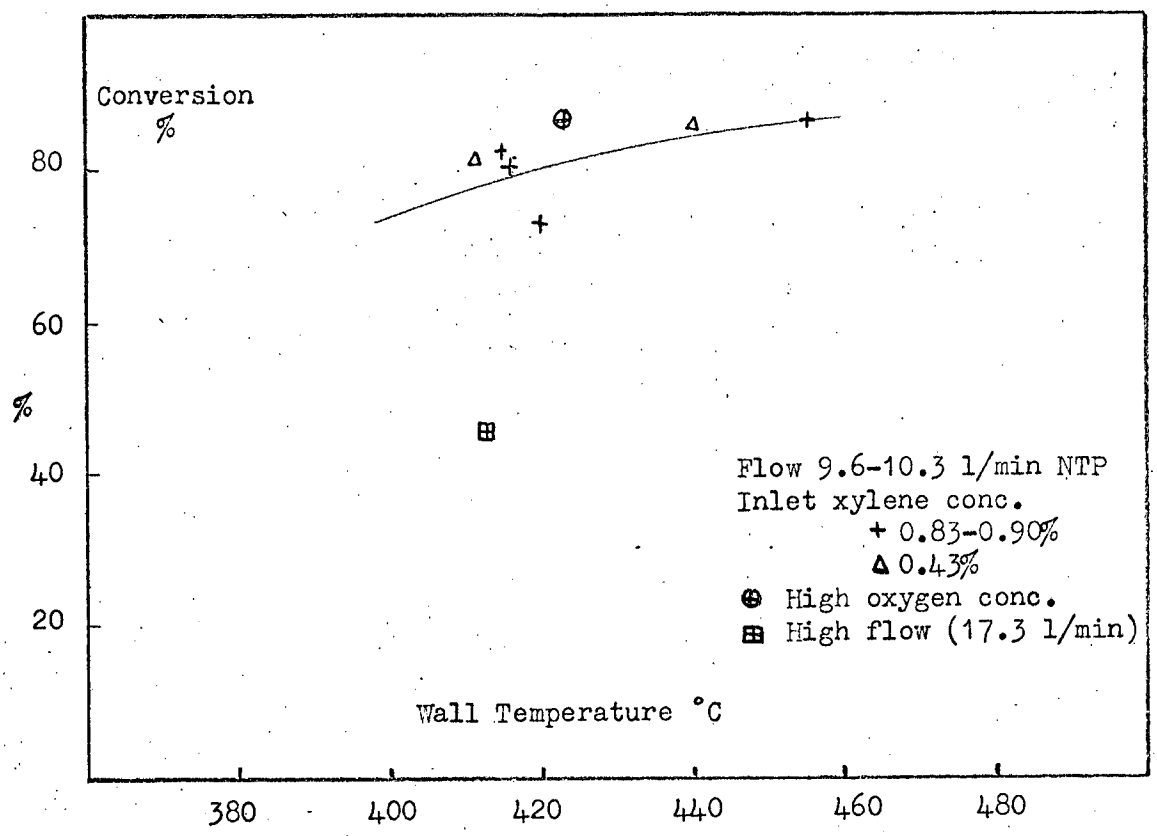
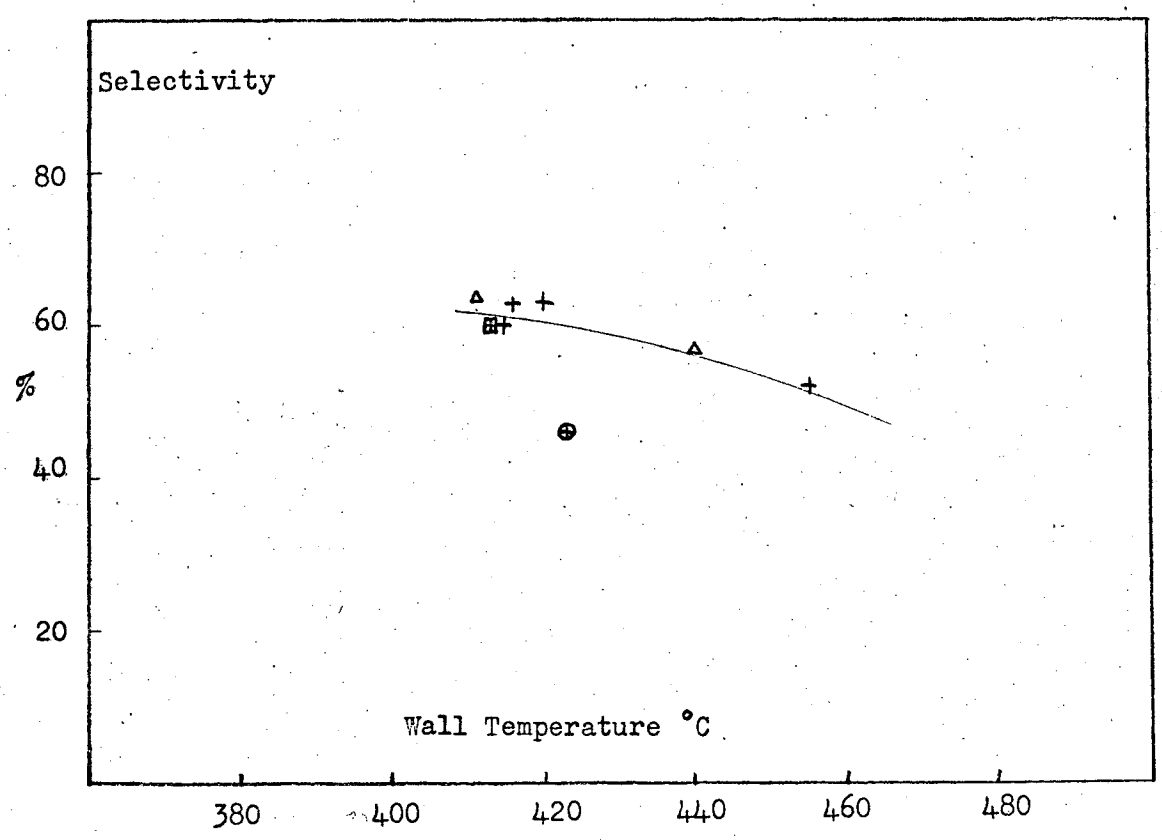


FIGURE 5.7 - CONVERSION and SELECTIVITY in the FIXED-BED REACTOR





found compared with a value of 55% at double the flowrate. Since the lowest flowrate corresponds to a residence time within the heated reactor volume (only $\frac{1}{3}$ of which contained catalyst) of approx. 6 seconds, comparable with the residence times in the C.S.T.R., it is probable that the lower selectivities are due in part to homogeneous combustion of phthalic anhydride, as found in the C.S.T.R. Because of the high temperatures in the fixed-bed (up to 600°C), catalytic combustion of phthalic anhydride might also be occurring.

Several runs were performed at the two higher flow rates with xylene inlet concentrations of half the normal 1% (approx.) value. While the levels of conversion were not significantly different, a decrease in the phthalic anhydride selectivity occurred at the lower flow. This decrease is apparent in Figure 5.6, where it will be seen that, while the selectivities at the 0.5% inlet concentration are significantly below the 1% inlet values at wall temperatures below 460°C, above this temperature the selectivities at the different inlet concentrations are tending to the same value. Since no such difference is apparent in the 0.5% and 1% inlet runs at the higher flow (figure 5.7), it can be concluded that the cause of the two levels of selectivity must be the different operating conditions at the lower flow - viz. the longer residence time or the lower temperature level of the bed.

If homogeneous product combustion was occurring to a significant extent at the lower flow, the change in selectivity could be explained by the assigning of concentration dependencies to the phthalic anhydride formation and homogeneous combustion rates such that a reduction in the formation rate (due to halving the xylene concentration) would be accompanied by a relative

increase in the homogeneous combustion rate. It would be necessary only to make the homogeneous combustion less dependent on the phthalic anhydride concentration than the formation reaction is dependent on the xylene concentration. Although Figs. 5.6 and 5.7 show that the selectivities in the 1% inlet runs at both flowrates are not significantly different, it cannot be positively concluded from this that homogeneous reactions do not occur to a greater extent at the lower flow, since the higher flow runs were conducted at higher catalyst bed temperatures, and so any potential improvement in selectivity due to a reduction in residence time may have been offset by catalytic combustion at the higher temperatures.

As one would expect from Figs. 5.3 and 5.4, a decrease in both the flow and the xylehe inlet concentration greatly lowers the general bed temperature level. The 0.5% inlet runs in Figure 5.6 had maximum measured temperatures of only 40°C (approx.) above the wall temperature. It is known that o-xylene reacts to phthalic anhydride via several intermediates (see Chapter 1), and it is possible that the activation energies of the intermediates' reactions are such that an increasing temperature sequence favours their reaction to phthalic anhydride while isothermal conditions favour their complete combustion. If this is the case, as the bed temperature peak was reduced, one would expect a decrease in selectivity. This suggests that the lower selectivities observed in the C.S.T.R. were due in part to the isothermality of that reactor, as well as to homogeneous combustion of product.

It is not possible to decide which, if either, of these two possible explanations for the lower selectivities is valid without further experimental investigation.

Two runs were performed with carrier gas other than air, containing 12% and 39% oxygen, to investigate the effect of changes in the oxygen concentration. The results are summarised in Table 5.1.

Table 5.1

Effect of Variation of the Oxygen Concentration.

Run	Flow	Xylene inlet conc.	Oxygen conc. inlet	outlet	Conv.	Select.	T.wall
FXB.	l/min (NTP)	%	%		%	%	°C
26	10.4	0.83	20.8	17.0	79.7	63.2	416
27	9.7	0.90	12.5	8.2	82.1	60.3	415
28	9.7	0.89	39.2	33.4	85.9	46.4	423

For comparison purposes, the nearest run using an air/xylene feed is included. A reduction of the oxygen concentration of approx. 50% had no significant effect on the results. When an attempt was made to repeat the run with an oxygen inlet concentration of 39%, a much more rapid rise in the bed temperature was observed, and a slow rise in the wall temperature occurred. The maximum measured steady-state temperature was 173°C above the wall temperature, compared with 119°C in the air run. It was found that while

there had been a slight increase in the conversion, the selectivity was markedly poorer. It therefore appears that at least one of the combustion reactions is oxygen dependent.

The results are generally similar to those obtained by Caldwell, who concluded that, at wall temperatures in the range 390°C - 430°C, a yield of phthalic anhydride of approx. 60-65% was obtained and was virtually independent of flowrate, catalyst dilution, and xylene feed concentration. It should be noted that his residence times were always less than in this study, his temperature profiles in the undiluted and diluted runs were much sharper than here, and he varied his xylene inlet concentration by only ± 30%. He employed an air feed throughout. The main differences found in this study - viz. lower selectivities at longer residence times and higher wall temperatures, and at the low xylene inlet concentration - are most probably due to the occurrence of homogeneous combustion and/or the less severe temperature profiles.

5.5 Catalyst Colour Changes

It was reported in Chapter 3 that, irrespective of the colour mixture of catalyst pellets placed in the C.S.T.R. basket, all the pellets had the same colour after a run. It was found that the pellets in the fixed-bed were, after use, of mainly two quite different colours - either a slightly darker yellow than the fresh catalyst or a virtually-black colour. Because of the difficulty in removing catalyst from the fixed-bed, it was not possible to decide whether one or other of these colours occurred predominantly at the "hot-spot", but it was possible to observe that the colour changes were quite

local, so that frequently two adjacent pellets were of different colours.

As similar rates were obtained in the C.S.T.R. with pellets of both colours, it is thought unlikely, however, that these colour changes are of significance.

5.6 Catalyst Activity

Caldwell found that his steady-state temperature profiles were not reproducible and he concluded that this was due to variable catalyst activity. However, the profiles in this reactor were easily reproducible. The series of fixed-bed runs was interrupted for several weeks while the reactor was being run in the fluidised-bed mode, and during this time the fixed-bed catalyst was left in the laboratory air. When it was returned to the reactor, it exhibited the same activity as before.

In view of the difficulty previously described in activating the catalyst on heating from room temperature to temperatures less than 390°C in the C.S.T.R. runs, it was thought initially that the difference in reproducibility was due to the different mode of operation of the two fixed-bed reactors. Because of the potential leak problem due to thermal expansion effects, described in Chapter 2, this reactor was maintained at approx. 400°C when runs were not being performed, whereas Caldwell returned his reactor to room temperature after almost every run.

However, Ellis (90) has reported that, using Caldwell's reactor but with an improved product collection system, he obtains reproducible profiles with the same mode of operation.

It is probable that Caldwell's temperature fluctuations were caused by

flow fluctuations, in turn caused by changes in the pressure drop in his collection system. Caldwell believed that the two thermocouples which showed the greatest fluctuations were situated on the shoulders of his very sharp temperature peak, and so were hyper-sensitive to even minor changes in any system variable.

5.7. The Behaviour of Caldwell's Reactor

Caldwell concluded that the dynamic behaviour of his reactor indicated an abrupt variation in the reaction state akin to the ignition and extinction of a flame, albeit much less pronounced. By the choice of reasonable values for mass and heat transfer coefficients and the use of Froment's[12] kinetic data for xylene disappearance, Caldwell was able to calculate an extinction/ignition range of approx. 30° above that he estimated experimentally from his data. Since the actual rate of xylene disappearance on this catalyst is slightly more rapid, this difference can be reduced further. This must be considered as good qualitative agreement between theory and experiment.

However, Caldwell then sought to explain four further features of his work, not explained by the transport effects, by modifying his theory to allow for surface reoxidation of the catalyst. He explained the four features thus:

a) Colour changes in the catalyst as due to varying oxidation states.

b) Lack of reproducibility in the temperature profiles to the fact that the catalyst activity was a variable quantity determined by the prehistory of the reactor.

c) Failure of the reactor to perform below 380° (approx.) to the fact the catalyst was then largely in a reduced condition.

d) Independence of the temperature profile on the bulk xylene partial pressure in the induction period by the fact that here reoxidation of the catalyst was rate-controlling.

As discussed in section 5.5, the colour changes do not seem significant as regards catalyst activity. It is believed that his temperature non-reproducibility was due to flow fluctuations. Since catalysts generally have a defined operating range, explanations other than a reduced oxide state can account for the inactivity, eg. lattice defect immobility. (83)

Although Caldwell states that the temperature profile was independent of the xylene partial pressure in the induction state, the only results he presents of a run with a cut in the xylene feed suggest some doubt. His figure 30 clearly shows that his thermocouple 2, situated one foot from the reactor inlet rose by 2°C in the preceding four minutes before he made a cut of 54% in the xylene feed concentration. In the next four minutes it rose by less than 1°C. Since, in the induction period, the maximum excess temperature was only about 15°C, and because of the doubt about the magnitude and position of the hot-spot due to the permanent location of the thermocouples (his No.2 thermocouple was the first in the bed and was 18 inches from the next one), a change in the rate of a point temperature rise of even 1°C/four minutes must be considered significant.

Since the C.S.T.R. results were oxygen independent in their range of

391 - 432°C. Caldwell's modification is unnecessary.

It is of interest to note that colleagues engaged in the mathematical modelling of fixed-bed reactors have performed preliminary calculations using the kinetic data obtained in the C.S.T.R. and obtained encouraging qualitative agreement between their mathematical model and Caldwell's reactor.

Chapter 6

The Fluid-Bed Reactor Results

As stated in Chapter 1, only a preliminary investigation of the fluid-bed oxidation of o-xylene was made. To enable comparison of the results with those of the other two reactors, it was necessary to use the same catalyst. As the suppliers of the fixed-bed catalyst did not make the catalyst in a fludising form, it was decided to crush the pellets in a ball mill to a suitable size for fluidisation. This was done by an outside firm.

6.1 Catalyst Activation

Severe difficulty was encountered in obtaining any significant catalyst activity in the first 15 hours use. During this time attempts were made to oxidise a 1% xylene feed at wall temperatures up to 500°C. Conversions of (approx.) 10% were obtained, much less than expected from the C.S.T.R. results. The catalyst bed was operated in the fixed-bed mode, by reducing the gas velocity below the minimum fluidisation velocity, to investigate whether the imposition of a hot-spot made significant difference. The conversion was raised, but only to 15 - 25%, with selectivities of (approx.) 30%.

The wall temperature was progressively raised, as it had been found possible to activate fresh catalyst in the C.S.T.R. by heating it for a brief period (10 - 15 mins.) at 450°C. After the fluid-bed had been operating at a wall temperature of 590°C for over an hour, an increase in the catalyst activity occurred. When the temperature was reduced to the normal range, the

catalyst was found to exhibit greater activity than before, but still less than expected from the C.S.T.R. results. All the runs reported were performed with the catalyst in this state of activity. Possible reasons for the observed catalyst behaviour are discussed in section 6.4.3.

6.2 Range of Study

A total of 15 runs was performed; the catalyst was used for approx. 55 hours after it was activated. The range of variables employed was:

xylene inlet conc.	- 0.85%, 2.1%, 0.42%
oxygen inlet conc.	- Air, 12%, 40%
wall temperature	- 400 to 520°C.

Conversions of (approx.) 34 to 90% were obtained.

6.3 The Fluid-Bed Physical Behaviour

Experimentally, the minimum fluidisation velocity was found to lie between 0.8 and 1.2 cms/sec. at room temperature, corresponding to a flowrate of 1000 to 1500 cc/min. As this is about double the value calculated from the size distribution given in Chapter 2, it is probable that particle agglomeration was occurring. A flowrate of 10 l/min. (at N.T.P.), corresponding to a velocity of 20 cm/sec. at 400°C, was employed in all the runs, and was found to be sufficient to maintain a reasonable degree of isothermality in the bed. The measured temperature deviation across the bed never exceeded 3°C. Some carry-over of fines occurred in the initial few hours of operation, i.e. before activation, but losses soon became negligible; eg. less than 1 gm.

of catalyst was collected in the cyclone during the first three runs after activation compared with a weight of catalyst in the bed of 250 gms.

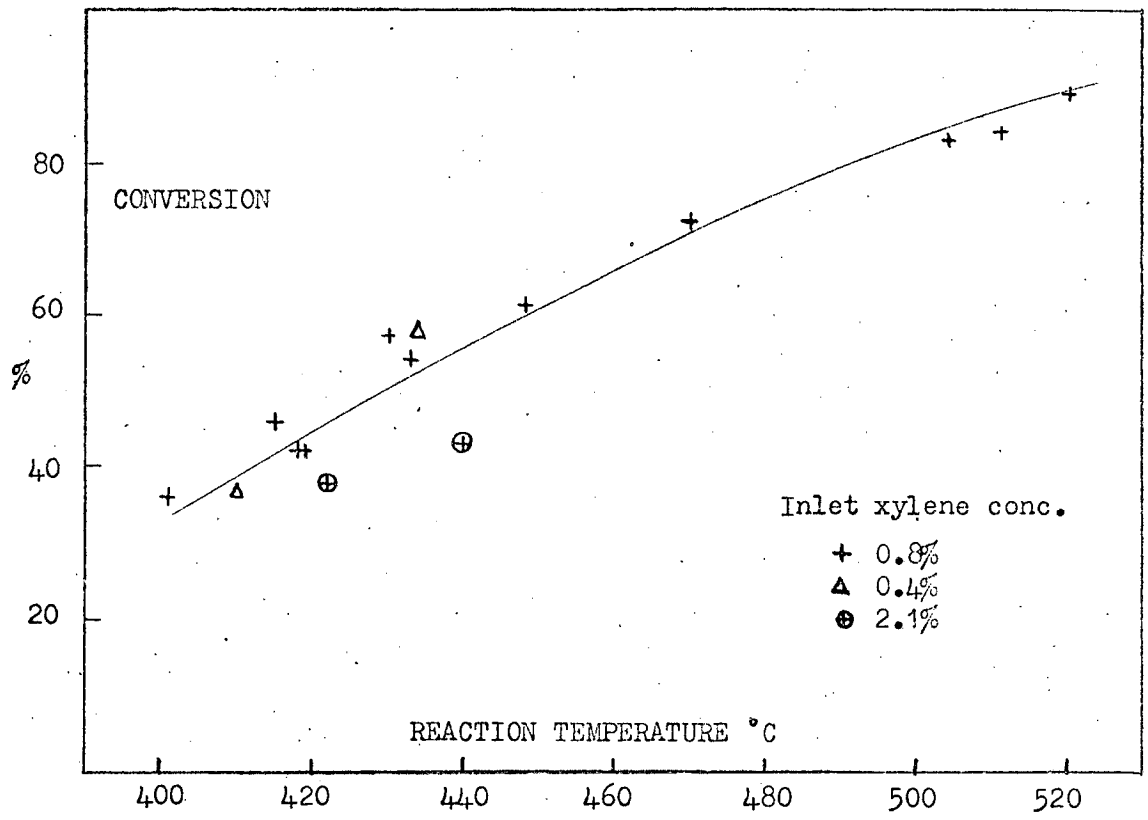
6.4 The Fluid-Bed Reactor Results.

The conversions and selectivities obtained in the 15 runs are presented in Figure 6.1, where it will be seen that, as the wall temperature was increased from 400 to 500°C, the conversion rose from 35% to 85%, while the selectivity remained approximately constant at 50%. Above 500°C, a decrease in the phthalic anhydride selectivity was apparent.

The rate of xylene disappearance was calculated from the C.S.T.R. data correlation at the outlet conditions of each of the fluid-bed runs, and the ratios of the actual fluid-bed rates to these theoretical rates are shown in Figure 6.2. For all the runs, the actual value of the rate was between 16 and 35% of the theoretical value. If the two high xylene inlet concentration runs (at 2.1%) are excluded, then, as the wall temperature increases, a slight decrease in the ratio of actual to theoretical rate becomes apparent. As the conversions in the two 2.1% xylene runs were less than 42% and as mixing is unlikely to have been perfect, it is probable that, for part of the catalyst bed, the xylene concentration would have been within the range found to cause catalyst deactivation in the C.S.T.R. Consequently, these two runs would be expected to show a lower relative rate than the others.

The conversion and selectivity were not significantly altered by either a decrease in the xylene inlet concentration from the normal 0.8% to 0.4%, or by a change in the oxygen concentration from 21% to (approx.) 12% or 40%. This

FIGURE 6.1 - CONVERSION and SELECTIVITY in the FLUID-BED REACTOR



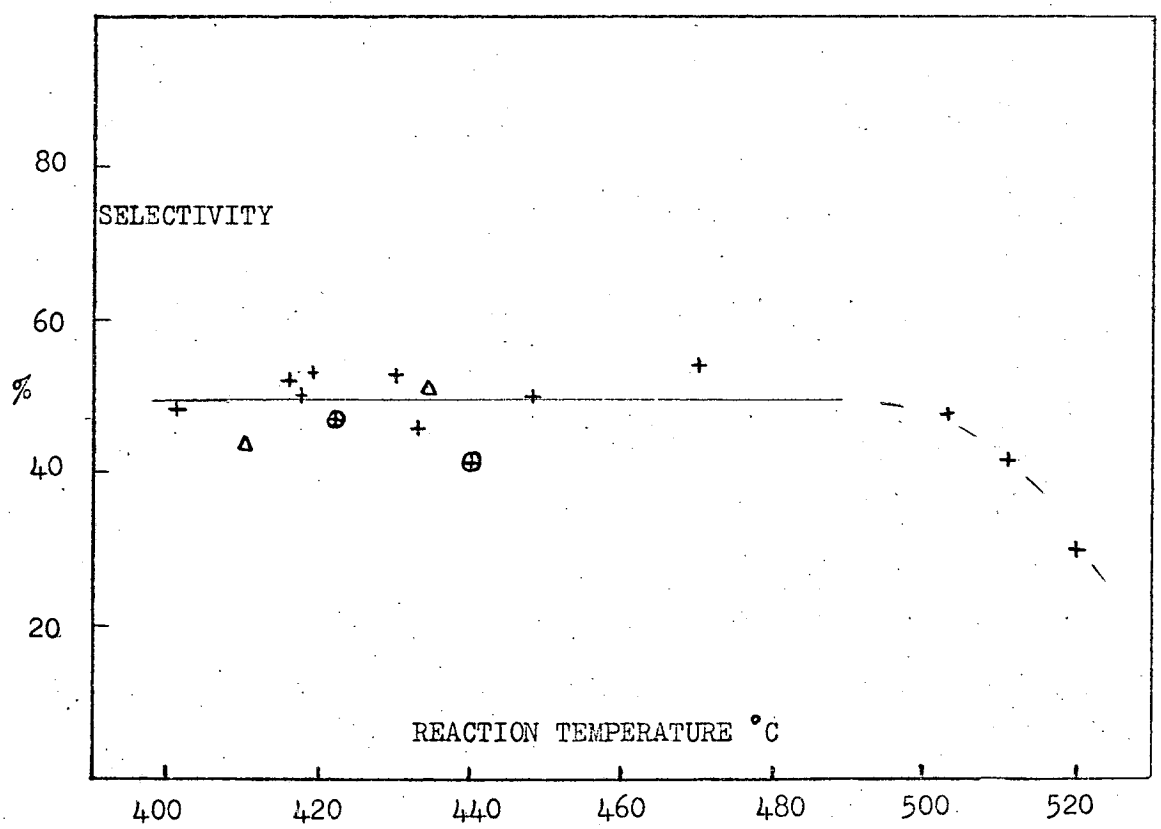
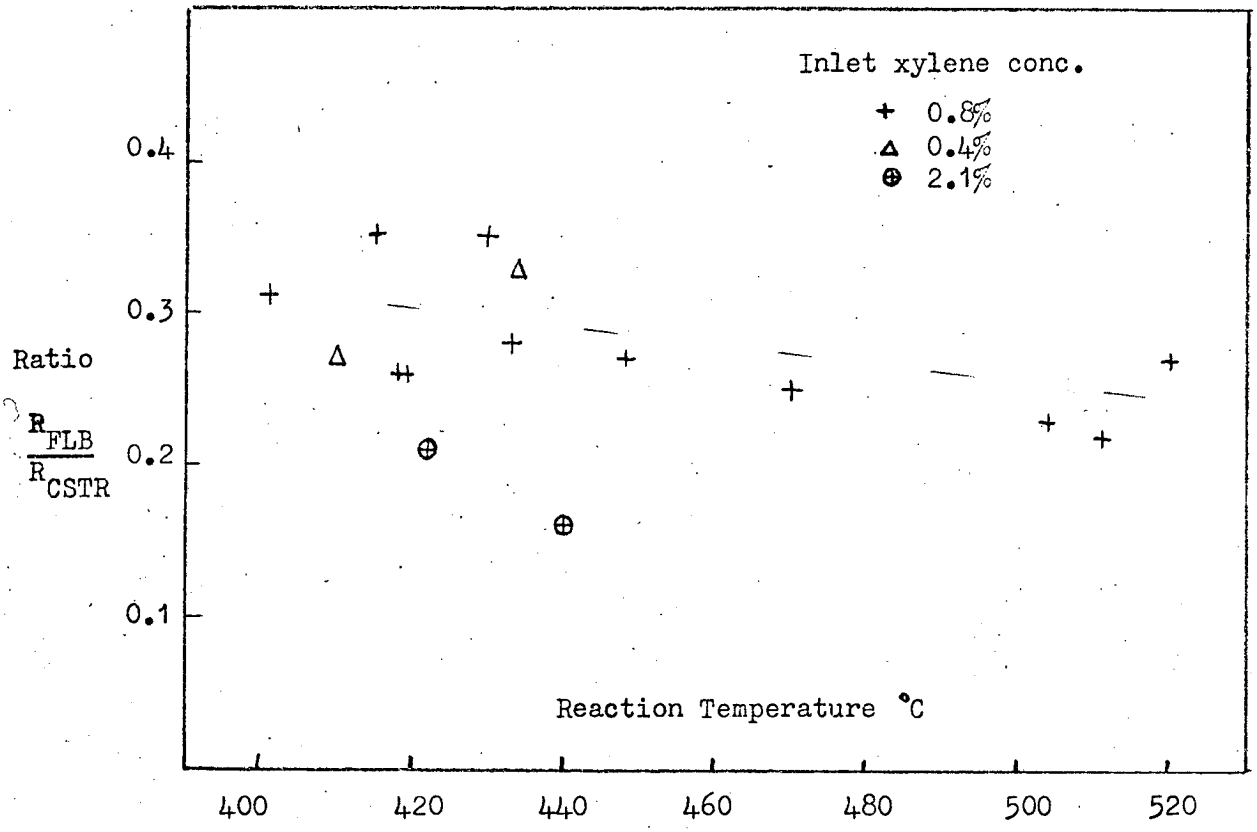


FIGURE 6.2 - RELATIVE RATES IN THE FLUID-BED REACTOR AND THE C.S.T.R.



Note : R_{FLB} has been calculated at the fluid-bed outlet conditions from the CSTR data correlation.

oxygen independence is demonstrated in Table 6.1.

It will be recalled that a similar increase in the oxygen concentration caused a significant decrease in the fixed-bed selectivity.

Table 6.1

Effect of Variation in Oxygen Concentration

Run FLUB.	% Oxygen (outlet)	Wall Temp. °C	Conv. %	Select. %
15	10.0	419	42	54
14	37.5	418	42	50
13	18.4	415	46	52

indicating the oxygen dependence of at least one of the combustion reactions. The fact that a similar decrease did not occur in the fluidised bed where homogeneous reactions would have been largely suppressed by the large surface area suggests that the reaction in question was homogeneous.

Three features, in particular, of the fluid-bed results require explanation, viz.:

a) the approximately constant selectivity, but lower than in the fixed-bed.

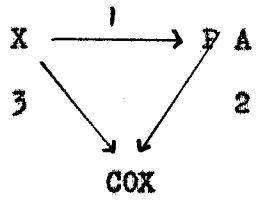
b) the decrease in the ratio of actual to theoretical rate as temperature increased.

c) the low level of catalyst activity.

Possible explanations for these are discussed in the following three sections, but because the kinetic study in the C.S.T.R. produced information about only the total xylene disappearance rate a degree of speculation has been necessarily employed.

6.4. 1. The Selectivity Level

If the simple triangular scheme of Froment is considered:



then a fluidised-bed reactor would normally be expected to give a lower selectivity than a fixed-bed if significant combustion of phthalic anhydride could occur, but the selectivity would be expected to vary with conversion, a feature not observed in this reactor.

The selectivity to phthalic anhydride may be obtained from the triangular scheme:

$$\text{Selectivity} = \frac{k_1.X - k_2.PA}{(k_1 + k_3).X}$$

$$= \frac{k_1 . X}{(k_1 + k_3).X} - \frac{k_2 . PA}{(k_1 + k_3).X}$$

Caldwell's constant selectivity in the fixed-bed reactor implies k_3 = constant k_1, and so the selectivity will remain constant if $k_2.PA/k_1.X$ remains constant. To obtain an estimate of the temperature dependency that this imposes on k_2, consider two of the fluid-bed runs near the temperature extremes of the observed constant selectivity:

Run	T	Conv.	Select.	X	PA
13	415°C	46%	52%	0.46%	0.20%
4	470°C	72%	54%	0.24%	0.33%

Using estimates for k_1 from the C.S.T.R. data, and the above concentrations, it can be calculated that a value for k_2 at 415°C of 0.59 times k_1 (at 415°C), and an activation energy for k_2 of (approx.) 5 kcal/mole produce the same selectivity at these two extreme runs.

It is suggested, therefore, that the lower and almost constant selectivity in the fluid-bed is due to phthalic anhydride homogeneous combustion, of the magnitude stated, the low temperature dependency being explained by extensive suppression of the homogeneous reaction by the large surface area in the reactor. The decrease in selectivity above 500°C is presumed to be caused by the onset of significant xylene homogeneous combustion.

The results can also be explained by a postulated change in the catalyst to a less selective oxide or by the adoption of a more complex reaction scheme

in which values of kinetic parameters are assigned to the reactions of the intermediates in such a way as to ensure a lower isothermal selectivity.

6.4.2 The Observed/Theoretical Rate Ratio.

The slight decrease in the ratio of the actual fluid-bed rate to that calculated from the C.S.T.R. data at fluid-bed outlet conditions as the reactor temperature rose is probably due to one of two causes:

a) the C.S.T.R. data when projected to the higher temperatures has been extrapolated beyond its range of accuracy.

b) at the higher temperatures, the fluid-bed rates are influenced by mass transfer effects.

If, for the catalytic surface area per unit mass, the highly conservative value of 4 $cm^2/gm.$ is taken (i.e. equal to the surface area of a sphere of the same diameter as the fixed-bed pellets), then $k_g a$ for the fluid-bed is at least thirty times greater than k_x, the xylene kinetic parameter, at 430°C. At 500°C, $k_g a$ is still at least seven times greater than k_x. As Caldwell quotes a value for the surface area of the fixed-bed catalyst pellets of approx. 0.2 $m^2/gm.$ (i.e. 500 times greater than the value used in the estimation of $k_g a$) one would not expect significant mass transfer limitations. However, since the lower activity observed in the fluid-bed may be due to loss of catalytic surface, mass transfer limitations remain a possibility.

6.4.3 The Low Catalyst Activity.

When it was decided to crush the catalyst pellets to a size suitable for fluidisation, it was assumed that, since the pellets were surface-coated, the catalytic area per unit mass would be unaltered. The low activity observed is indicative, however, of a loss of active catalyst. There are several possible causes of this loss:

a) physical loss of catalyst

b) surface contamination

c) existence of a major proportion of the catalyst in a non-active oxide state

d) loss through particle agglomeration

While some loss of catalyst may have occurred during the crushing process (eg. as fines), it is unlikely that any such loss would have been of the magnitude required to explain the disagreement between actual and theoretical rates. The fact that the catalyst was successfully activated at high temperature, but to a level still less than expected, suggests that possibilities (b) and (c) are more likely. If the catalyst surface had been contaminated during crushing, then the high temperature activation may have been due to the combustion, and thus removal, of the contaminant. The existence of the various levels of catalyst activity observed in the C.S.T.R. suggests the possibility of the catalyst being in a non-active oxide state, the high temperature activation being caused by a change in the oxide state through reaction with either the hydrocarbon or the oxygen.

Since particle agglomeration did occur, it is possible that it rendered

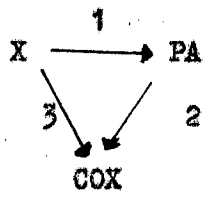
catalytic surface inaccessible to the reactants; because of the high temperature activation this possibility must be linked to either (b) or (c).

In view of the reported heterogeneous-homogeneous interaction reported in the case of benzene oxidation (73), it is of interest to consider whether the fluid-bed results are explicable by a similar mechanism. While the low phthalic anhydride formation rates could be caused by the partial suppression by the fluid-bed of a homogeneous step in the overall mechanism, the low xylene disappearance rate, if not due to loss of catalytic area, would be explicable only by the postulation of a scheme exactly analogous to that proposed for benzene oxidation, where a catalytically-formed intermediate is capable of reverting to o-xylene. Since, for phthalic anhydride formation, the oxygen attack of the xylene molecule must proceed via the methyl groups, the reversibility of any likely intermediate must be considered very unlikely. The results from all three reactors are inconclusive about the possible existence of a homogeneous step in the phthalic anhydride formation.

Chapter 7

The Overall Reaction Scheme.

As discussed in Chapter 1, the simplified triangular scheme of Froment adequately represents the oxidation of o-xylene on the "German" catalyst, i.e.



Although the kinetic study in the C.S.T.R. failed to produce quantitative data about the reaction system (other than the total xylene disappearance rate), the results from the different reactors are sufficient to permit comment on the applicability of this scheme to the oxidation on this "American" catalyst.

The xylene disappearance rate kinetic parameter k_x ($=(k_1 + k_3)$ on the triangular scheme) satisfied closely an Arrhenius equation, implying that the activation energies of steps 1 and 3 are approximately equal (or $k_3 \approx 0$). The independence of Caldwell's yield on the xylene concentration and the temperature profile strongly suggests a parallel scheme, with negligible phthalic anhydride combustion. The highest selectivity obtained in the 2 inch diameter fixed-bed reactor was virtually the same as Caldwell's value, and the homogeneous combustion of phthalic anhydride, which was demonstrated to be occurring to a large extent in the C.S.T.R., is believed to have been the major cause of the lower selectivities at the longer residence times in

the fixed-bed reactor and in the C.S.T.R.

It was shown in the last chapter how, in the fluid-bed reactor, the occurrence of phthalic anhydride homogeneous combustion (but to a lesser extent than in the fixed-bed due to partial suppression of the reaction by the bed surface area) could explain the lower selectivity in that reactor.

The results from the different reactors strongly suggest that the reaction on this catalyst can be represented by a triangular scheme similar to Froment's, but with the catalytic phthalic anhydride combustion step changed to one that is mainly homogeneous.

Such a homogeneous step would explain the improved yields obtained by the addition of potential radical suppressors (eg. B $(OEt)_3$ [21]) to the gas phase.

The failure of catalyst dilution to improve the yield indicates that no temperature constraint was reached in the operating range of the one inch diameter fixed-bed reactor i.e. no significant catalytic combustion of phthalic anhydride occurred at the "hot-spot". Caldwell's short contact time evidently eliminated homogeneous combustion, suggesting that phthalic anhydride homogeneous combustion has an induction period greater than the residence time in the one inch fixed-bed reactor but less than that in the two inch diameter reactor, i.e. between approx. 0.3 secs. and 1.5 secs. at 400°C. If the catalyst used in this study is indeed typical of the "American" type of catalyst, then there is a major difference in the rates of phthalic anhydride catalytic combustion on the two types of catalyst. While the rate of o-xylene observed in this study is of a similar magnitude to that obtained by an

extrapolation of the "German" kinetic data, the rate of phthalic anhydride oxidation on the "American" catalyst must be considerably less than that predicted from the "German" data.

While it is possible that the "German" kinetic rate for the catalytic combustion of phthalic anhydride has been overestimated due to the onset of homogeneous reaction at the longer residence times required by that type of catalyst, the rapid decrease in selectivity reported by Carra et al (33) from (approx.) 65% at 410°C to 35% at 460°C in a fluidised bed of the "German" catalyst suggests a large degree of catalytic combustion.

Chapter 8

Conclusions and Recommendations for Further Work

1. Over the range of conditions studied in the spinning-basket reactor the rate of o-xylene disappearance over a promoted V_2O_5 on SiC catalyst is adequately described by either

(a) a power law, first order in o-xylene, zero order in oxygen i.e.

$$R_X = k\, p_X$$

where $\ln k = \left(\frac{-26300}{RT} + 17.95\right)$ m/g.hr.atm.

or by

(b) a Hughes-Adams type equation i.e.

$$R_X = \frac{Ap_X}{1+Bp_X}$$

where $\ln A = (-26400/RT) + 18.14$ (m/g.hr.atm)

$\ln B = (3890/RT) - 0.003$ (atm^{-1})

2. The rates of catalytic combustion of reactant and products were inaccessible due to the occurrence of homogeneous reactions.

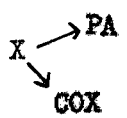
3. Above o-xylene partial pressures of 0.016 atm a reversible deactivation of the catalyst is apparent. It is suggested that this is due to a partial reduction of the catalyst. Approximately 5% of the experimental runs in the spinning-basket reactor exhibit the same trends as the majority but have a rate almost double that predicted by the correlations in Number 1. It is conjectured that this is caused by a change in the catalyst oxide structure.

4. At the shortest residence times employed in the fixed-bed reactor, the experimental results agree with those reported by Caldwell, viz. a selectivity to phthalic anhydride of 65% virtually independant of temperature and reactant concentration.

The lower selectivities observed at the longer residence times are believed due to phthalic anhydride homogeneous combustion.

5. The selectivity observed in the fluidised-bed reactor was less than that generally observed in the fixed-bed reactor, in accord with industrial experience. It has been speculated that this is due to partially-suppressed homogeneous combustion. The fluid-bed catalyst exhibited a low level of activity; although possible causes have been suggested, it was not possible to identify which, if any, was the true one.

6. The results from the three reactors and Caldwell's work strongly suggest the reaction may be represented by a parallel scheme:



with approximately equal activation energies for the two reactions. Homogeneous combustion of phthalic anhydride is believed to occur after an induction period of approximately one second.

Recommendations for Further Work

A degree of speculation has been necessary in the consideration of the results because only the kinetics of xylene disappearance were measured. Before further kinetic study is undertaken, two features of the present work should be modified:

a) the outlet xylene should be measured, not calculated.

b) homogeneous product combustion should be prevented.

The partial success of direct sampling into a chromatograph suggests that further development of this technique will solve (a).

The homogeneous combustion can be prevented by reduction of the residence time to considerably below a second or by the addition of free radical chain terminators. The former suggests the use of a different reactor system; the latter is not recommended in view of the findings of Trimm concerning the existence of a homogeneous step in the formation of maleic anhydride. It is suggested that a study be undertaken to discover whether there is a similar homogeneous formation step in phthalic anhydride formation from naphthalene or o-xylene.

While the rate of o-xylene disappearance over this "American" type catalyst is of the same order as that found over the "German" type, it is apparent that phthalic anhydride catalytic combustion on the former is insignificant.

A study of this reaction over the two types of catalyst may therefore highlight the differences between the two types and thus illuminate some aspects of catalyst behaviour, while at the same time providing useful kinetic data.

The fixed-bed experiments were conducted largely at high conversion, and so little is known about the selectivity to phthalic anhydride at low conversions. Although the fluid-bed results suggest that the selectivity is independent of conversion over the range studied, these experiments cannot be assumed to be representative of the normal catalyst behaviour because of the low level of catalyst activity. A series of experiments conducted in a fixed-bed reactor at low conversion would permit quantification of the extent of direct xylene catalytic combustion and would enable the applicability of the parallel reaction scheme to be investigated.

NOMENCLATURE

A, B	Rate constants in the Hughes-Adams equation (A - m/g hr atm, B - atm^{-1})
a	surface area of catalyst per unit mass (cm^2/g)
C	concentration of reactant (m/ℓ)
E	Activation energy (kcal/mole)
ΣE^2	sum of the squared error of the reaction rates
ΔG	Gibbs Free Energy change (kcal/mole)
ΔH_1, ΔH_1^*	Heats of adsorption (kcal/mole)
ΔH_2, ΔH_2^*	Heats of desorption (kcal/mole)
K	Adsorption Equilibrium constant
k	
k_1, k_2, k_3	rate constants (usually m/g.hr.atm)
k_1, k_{-1}, k_2	
k_o	pre-exponential factor in Arrhenius equation
k_g	mass transfer coefficient
k	conversion factor in Hughes-Adams eqn.
P	total pressure or xylene vapour pressure
p	partial pressure of reactant
R	reaction rate (m/g.hr)
ΔS	Entropy change for reversible adsorption (cal/m^oC)
S	Selectivity
s	moles of oxygen consumed per mole of hydrocarbon converted
T	temperature (^oC or ^oK)
T_w	wall temperature (^oC)
θ	fraction of catalyst surface covered by oxygen

Subscripts

a	oxygen (with k only)
calc	calculated value
N	hydrocarbon
o	oxygen
PA	phthalic anhydride
X	o-xylene

Superscripts

a, b, n	orders of reaction

Abbreviations used for Chemical Substances

COX	carbon oxides
MA	maleic anhydride
oMBA	o-methylbenzyl alcohol
PA	phthalic anhydride
PI	phthalide
TA	o-tolualdehyde
TAc	o-toluic acid
X	o-xylene

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APPENDIX 1

Mass Balance Equations

Let the flowrates (in gm moles/min) of the chemical substances be as follows:

Into Reactor	(moles/min)	Out of Reactor	(moles/min)
o-Xylene	a	o-Xylene	d
Oxygen	b	Oxygen	e
Nitrogen	c	Nitrogen	f
		Phthalic anhydride	g
		Phthalide	h
		o-tolualdehyde	i
		Carbon dioxide	j
		Carbon monoxide	k
		Water	l

The reactions which occur in the reactor may be represented by the following five equations for the purposes of mass balance determination:

$$\underset{(o\text{-}X)}{C_8H_{10}} + 3O_2 \longrightarrow \underset{(PA)}{C_8H_4O_3} + 3H_2O \qquad (1)$$

$$C_8H_{10} + 2O_2 \longrightarrow C_8H_6O_2 + 2H_2O \qquad (2)$$
(pide)

$$C_8H_{10} + O_2 \longrightarrow \underset{(Tol)}{C_8H_8O} + H_2O \qquad (3)$$

$$C_8H_{10} + 10.5\,O_2 \longrightarrow 8CO_2 + 5H_2O \qquad (4)$$

$$C_8H_{10} + 6.5O_2 \longrightarrow 8CO + 5H_2O \qquad (5)$$

The number of moles of o-xylene which react to organic products is known directly from the product collection.

Let x and y moles of o-xylene react to CO_2 and CO respectively. The exit reactor stream then becomes:

The o-xylene input to the reactor was calculated using the equations

$$\text{moles Xylene/min} = \frac{\text{Vap}}{\text{Totp} - \text{Vap}} \times \text{air flow to bubbler}$$

where Vap = o-xylene vapour pressure at the temperature of the bubbler, and Totp = total pressure, always taken as atmospheric pressure.

The results of the mass balance calculations are presented in the subsequent sections of the Appendix.

APPENDIX 2

The C.S.T.R. Results

The experimental results obtained in the C.S.T.R. are presented in this section. Each run has been given a code symbol to distinguish between those used for determination of kinetic parameters and other runs. The symbols stand for:-

K - runs used for determination of kinetic parameters

A - Tail gas addition

B - Tail gas addition, having had CO_2 removed

C - CO_2 addition

DA - Runs performed generally at high concentration where a deactivation was observed

LR - Runs with abnormally low rates

HR - Runs with abnormally high rates

The composition of the catalysts is given in Chapter 2; the weights of catalyst loaded into the reactor were:-

Catalyst 1	Sample 1A	2.458 gms
	1B	2.712 gms
	1C	3.194 gms
	1C1	1.706 gms
2		2.607 gms
3		2.193 gms

Sample 1C1 was part of sample 1C.

CODE	RUN NO.	CATALYST	REACT TEMP °C	INLET FLOWS (N/MIN) XYL 6 ×10	OXY 5 10	NIT 5 10	GAS ANALYSIS CO2 %	OXY %
-	1	1A	404	78	117	440	-	16.3
-	2	1A	404	433	108	407	-	12.9
-	3	2	396	136	67	252	4.81	12.4
-	4	2	374	120	61	228	1.58	18.1
-	5	2	392	120	61	229	4.22	12.6
-	6	2	423	139	69	258	9.00	6.2
-	7	3	353	70	74	279	1.02	19.6
-	8	3	386	68	74	276	1.98	17.8
-	9	3	405	42	44	167	3.50	15.2
-	10	3	420	44	50	189	3.42	15.1
K	11	1B	411	378	361	1359	2.69	15.8
K	12	1B	411	154	235	883	2.66	16.8
K	13	1B	411	207	534	953	2.16	32.5
K	14	1B	411	108	222	834	1.90	18.0
K	15	1B	411	164	197	984	2.74	12.2
K	16	1B	411	309	295	1110	3.20	15.9
K	17	1B	411	61	108	405	4.71	14.1
K	18	1B	411	65	91	343	5.48	13.2
K	19	1B	411	100	201	757	2.28	17.4
K	20	1B	411	184	128	856	3.38	7.3
K	21	1B	411	211	287	1079	2.06	17.3
HR	22	1B	411	205	269	1010	3.63	14.9
HR	23	1B	411	207	269	1010	3.66	14.9
HR	24	1B	411	225	274	1029	3.77	14.7
K	25	1B	411	441	547	2059	1.22	18.3
HR	26	1B	411	198	268	1008	3.43	14.9
HR	27	1B	411	182	264	994	3.25	15.4
K	28	1B	411	186	227	1071	2.20	13.8
HR	29	1B	411	133	97	1085	2.57	2.6
K	30	1B	411	205	181	983	2.31	11.3
K	31	1B	411	225	287	1081	3.61	15.3
HR	32	1B	411	275	326	1225	2.96	15.8
HR	33	1B	411	170	298	1122	2.66	16.6
K	34	1B	391	149	219	823	1.91	17.9
K	35	1B	391	167	332	1249	0.88	19.5

RUN NO.	OUTLET FLOWS XYL	OXY	PA	PI	TOL	CO2	H2O	CO	CONV	SCTY	RATE	P XYL	P OXY
	MOLES PER MIN.							%	%	%	M/GHR	ATM.	ATM.
	$\times 10^{6}$	10^{5}	10^{7}	10^{7}	10^{7}	10^{6}	10^{6}				10^{5}	10^{2}	10^{2}
1	33	90	224	14	21	152	167	---	57.5	49.9	109	0.59	15.82
2	354	69	307	35	192	205	247	---	18.3	38.8	193	6.29	12.33
3	95	40	140	0	49	167	157	1.2	30.2	34.1	95	2.82	11.82
4	109	54	30	0	22	50	36	-1.1	8.5	29.8	23	3.64	17.88
5	73	37	183	29	33	130	153	1.2	35.1	43.3	97	2.56	11.97
6	50	20	117	0	374	312	271	0.5	64.0	13.1	204	1.44	5.91
7	60	70	14	0	67	35	21	-3.5	14.2	13.5	27	1.67	19.49
8	51	63	25	0	52	72	58	0.2	24.6	15.0	46	1.43	17.51
9	27	32	9	0	17	77	65	6.0	35.4	5.8	40	1.23	14.75
10	28	36	17	0	0	85	77	8.3	36.5	10.7	44	1.12	14.63
11	240	273	468	47	123	478	533	3.8	36.5	33.9	305	1.35	15.37
12	74	186	444	0	54	302	293	-4.5	52.2	55.1	178	0.65	16.37
13	119	481	477	0	71	326	318	-3.5	42.7	53.9	196	0.79	31.84
14	59	189	240	0	12	203	193	-1.3	45.5	48.7	109	0.55	17.63
15	83	143	317	0	57	330	316	1.1	49.2	39.4	178	0.69	11.85
16	192	221	663	0	45	466	434	-3.9	37.9	56.7	259	1.34	15.40
17	19	71	72	0	16	247	189	3.6	68.8	17.2	93	0.36	13.62
18	23	56	132	0	0	243	185	-1.9	64.8	31.1	94	0.59	12.62
19	49	166	222	0	20	222	204	-0.7	51.2	43.3	113	0.50	17.04
20	101	72	344	0	42	341	330	1.0	45.2	41.4	184	1.00	7.08
21	117	235	553	0	81	287	327	-2.5	44.5	58.8	208	0.84	16.93
22	88	189	478	0	67	475	465	1.8	57.2	40.7	268	0.67	14.41
23	76	187	614	0	119	479	487	-0.8	63.4	46.7	291	0.58	14.31
24	102	189	484	0	79	504	490	1.9	54.9	39.2	273	0.76	14.16
25	314	478	437	155	132	326	446	3.0	28.7	34.6	280	1.18	17.96
26	81	189	448	0	66	449	469	4.8	59.0	38.3	259	0.62	14.41
27	58	190	645	0	96	417	453	-1.1	68.3	51.9	275	0.45	14.85
28	102	178	479	0	66	294	298	-3.8	45.3	56.9	186	0.77	13.53
29	35	30	291	0	39	313	417	19.5	73.6	29.6	217	0.29	2.48
30	100	130	462	77	200	274	326	-1.9	51.0	44.2	231	0.84	10.97
31	128	208	161	26	53	507	428	4.6	43.4	16.4	217	0.91	14.80
32	120	242	681	101	214	470	519	-1.5	56.1	44.2	341	0.76	15.28
33	63	234	500	54	67	384	388	-2.2	62.6	47.0	235	0.44	16.19
34	94	186	256	38	40	202	194	-2.8	36.8	47.0	121	0.89	17.58
35	125	308	180	35	52	140	142	-1.4	25.1	43.0	93	0.78	19.29

NOTE: CO =% OF INLET XYLENE WHICH MUST REACT TO CO TO GIVE A MASS BALANCE

CODE	RUN NO.	CATALYST	REACT TEMP °C	INLET FLOWS (M/MIN) XYL 6 x10	OXY 5 10	NIT 5 10	GAS ANALYSIS CO2 %	OXY %
K	36	1B	391	115	219	822	1.40	18.8
K	37	1C	391	104	218	821	1.47	18.7
LR	38	1C	391	82	149	562	0.66	19.7
LR	39	1C	391	95	149	562	0.87	19.4
K	40	1C	391	143	329	1236	0.94	19.3
K	41	1C	391	33	201	756	0.72	19.8
K	42	1C	391	32	220	829	0.37	20.3
K	43	1C	391	85	114	429	4.73	14.3
K	44	1C	411	72	265	997	1.09	19.2
K	45	1C	391	45	240	903	0.75	19.8
K	46	1C	391	110	265	997	1.04	19.3
K	47	1C	411	65	303	1141	1.05	19.5
K	48	1C	391	66	251	944	1.52	18.9
K	49	1C	391	38	324	752	0.45	29.3
K	50	1C	411	40	324	751	1.07	28.6
K	51	1C	411	84	208	478	3.03	25.0
K	52	1C	411	44	144	700	1.24	15.4
K	53	1C	411	75	102	631	2.62	9.7
K	54	1C	391	34	73	513	1.09	10.4
K	55	1C	391	59	101	524	2.07	13.3
K	56	1C	411	38	99	513	2.15	13.3
K	57	1C	411	89	98	793	2.31	7.5
K	58	1C	411	183	237	892	2.79	16.3
K	59	1C	411	151	226	905	2.78	15.5
K	60	1C	391	59	202	813	1.00	18.3
K	61	1C	432	100	163	613	5.10	14.0
K	62	1C	432	117	264	663	5.05	21.6
K	63	1C	432	154	255	620	5.58	21.1
K	64	1C	432	133	221	830	3.85	15.6
K	65	1C	432	136	219	824	4.07	15.3
K	66	1C	432	117	206	774	4.14	15.2
K	67	1C1	432	56	138	520	3.60	16.2
K	68	1C1	432	67	350	382	2.78	43.8
K	69	1C1	432	85	344	375	3.30	42.7
C	70	1C1	432	94	140	527	7.28	10.0

RUN NO.	OUTLET FLOWS XYL	OXY	PA	PI	TOL	CO2	H2O	CO	CONV	SCTY	RATE	P XYL	P OXY
	MOLES PER MIN.							%	%	%	M/GHR	ATM.	ATM.
	6 x10	5 10	7 10	7 10	7 10	6 10	6 10				5 10	2 10	2 10
36	74	195	208	29	37	148	143	-3.8	36.1	50.1	92	0.70	18.51
37	61	194	213	36	46	154	145	-5.2	41.6	49.1	81	0.58	18.48
38	71	141	16	0	11	47	43	3.1	13.6	14.1	1	0.98	19.52
39	81	139	26	0	18	63	59	2.1	14.9	18.1	1	1.12	19.21
40	104	303	100	26	43	149	149	2.2	27.1	25.8	73	0.66	19.13
41	16	189	38	16	16	70	66	3.9	51.6	22.5	32	0.17	19.68
42	22	214	14	7	16	39	39	4.7	31.9	14.3	19	0.20	20.26
43	34	77	62	47	79	263	195	-1.1	60.0	12.1	95	0.61	13.77
44	32	242	148	31	52	138	139	-0.7	55.6	37.1	75	0.25	19.01
45	28	227	8	19	19	86	71	4.0	38.0	4.5	32	0.24	19.72
46	76	244	119	25	41	133	124	-0.7	31.2	34.5	64	0.59	19.11
47	30	281	117	29	31	153	127	-3.8	52.9	34.0	64	0.21	19.31
48	53	225	34	32	49	183	130	-1.3	38.5	10.3	62	0.44	18.70
49	24	316	20	19	24	49	51	4.4	36.9	14.2	26	0.22	29.18
50	15	306	41	24	24	116	97	2.5	61.4	16.9	46	0.14	28.31
51	27	170	160	40	46	213	226	7.8	68.4	27.7	109	0.38	24.21
52	22	129	69	16	22	105	79	-6.0	48.7	32.6	40	0.26	15.24
53	28	70	181	24	32	195	180	-1.1	62.5	38.3	89	0.38	9.47
54	10	60	119	20	25	64	81	-0.7	71.2	49.4	45	0.17	10.23
55	31	83	59	37	56	131	96	-5.5	47.8	21.0	53	0.49	13.13
56	14	81	63	15	18	132	96	-5.7	63.1	26.3	45	0.23	13.11
57	37	66	224	31	54	208	186	-5.2	58.5	42.8	98	0.41	7.33
58	96	183	323	62	78	322	322	0.3	47.7	37.0	164	0.83	15.84
59	75	174	235	47	64	321	295	1.2	50.6	30.7	144	0.65	15.12
60	35	186	59	20	37	102	88	-0.6	40.8	24.6	45	0.34	18.19
61	27	106	194	47	44	403	296	-5.5	73.2	26.4	138	0.34	13.47
62	29	196	224	57	52	477	357	-4.2	75.3	25.4	165	0.31	20.78
63	48	189	323	74	83	500	409	-3.1	68.6	30.6	199	0.54	20.12
64	47	162	305	44	97	410	320	-7.0	65.0	35.3	163	0.44	15.18
65	49	157	291	52	77	432	333	-6.3	64.1	33.3	164	0.46	14.84
66	36	146	274	30	54	413	321	-5.3	69.1	33.7	153	0.36	14.69
67	15	105	73	30	44	240	167	-5.4	74.0	17.5	146	0.22	15.82
68	23	318	58	31	60	207	173	4.1	65.3	13.4	153	0.31	42.75
69	35	305	55	35	55	243	210	6.8	59.4	10.9	178	0.47	41.53
70	10	66	80	33	47	621	378	5.2	89.6	9.4	159	0.14	9.50

CODE	RUN NO.	CATA LYST	REACT TEMP °C	INLET FLOWS (M/MIN) XYL 6 ×10	OXY 5 10	NIT 5 10	GAS ANALYSIS CO2 %	OXY %
C	71	1C1	432	125	362	380	7.40	37.6
K	72	1C1	432	81	361	389	3.57	43.1
K	73	1C1	432	143	228	858	3.17	16.6
A	74	1C1	432	102	206	841	1.40	17.2
B	75	1C1	432	110	204	827	0.92	17.8
K	76	1C1	432	122	213	801	2.78	17.0
K	77	1C1	432	137	223	841	3.22	16.5
K	78	1C	432	126	190	714	4.87	13.4
K	79	1C	432	208	272	717	5.23	18.3
A	80	1C	432	214	253	723	6.13	15.5
B	81	1C	432	201	247	714	4.41	17.5
K	82	1C	432	179	172	716	5.04	10.3
A	83	1C	432	187	157	714	5.90	7.4
B	84	1C	432	180	158	721	4.90	9.1
K	85	1C	432	246	301	731	5.94	19.0
A	86	1C	432	241	293	746	6.23	17.4
B	87	1C	432	261	290	745	5.09	18.0
K	88	1C	432	243	214	805	6.13	10.4
K	89	1C	432	233	214	805	6.20	10.3
DA	90	1C	432	373	268	1008	3.65	13.7
DA	91	1C	432	386	226	851	5.68	10.7
DA	92	1C	432	329	183	905	4.98	9.4
DA	93	1C	432	338	238	947	6.53	11.4
DA	94	1C	432	257	196	739	5.62	12.2
DA	95	1C	399	111	211	795	1.52	18.7
K	96	1C	399	116	184	754	1.60	16.7
K	97	1C	399	119	191	901	1.34	14.9
K	98	1C	399	163	244	919	1.41	18.1
K	99	1C	399	130	187	865	1.82	14.2
K	100	1C	399	122	357	767	0.95	29.4
K	101	1C	399	166	225	845	1.68	17.3
K	102	1C	399	135	218	908	1.43	16.7
K	103	1C	399	158	186	866	1.82	14.1
K	104	1C	399	173	349	770	1.05	28.1
K	105	1C	399	146	237	891	1.31	18.4

RUN NO.	OUTLET FLOWS XYL	OXY	PA	PI	TOL	CO2	H2O	CO	CONV	SCTY	RATE	P XYL	P OXY
	MOLES PER MIN.							%	%	%	M/GHR	ATM.	ATM.
	6 x10	5 10	7 10	7 10	7 10	6 10	6 10				5 10	2 10	2 10
71	24	278	68	43	99	685	438	6.1	80.6	6.7	189	0.31	35.54
72	31	321	56	33	45	273	211	3.1	62.1	11.1	176	0.40	41.93
73	71	179	229	37	102	350	267	-5.3	50.8	31.4	256	0.64	16.19
74	65	181	92	15	41	233	144	3.2	36.0	25.1	129	0.61	16.93
75	72	184	128	21	56	96	133	4.4	34.1	34.2	132	0.69	17.54
76	55	171	229	40	105	286	237	-4.7	55.3	34.0	237	0.53	16.58
77	62	174	244	46	116	346	270	-6.1	55.2	32.2	267	0.57	16.10
78	35	119	179	33	59	452	365	5.7	71.9	19.7	170	0.38	12.82
79	66	178	486	68	105	536	553	4.7	68.5	34.1	268	0.64	17.35
80	70	149	392	61	86	705	590	5.5	67.4	27.2	271	0.68	14.57
81	63	165	545	94	117	438	516	4.2	68.9	39.3	261	0.63	16.56
82	47	90	401	94	151	463	490	5.1	73.7	30.5	247	0.51	9.89
83	49	63	364	73	120	618	547	7.8	73.6	26.4	259	0.54	6.92
84	52	79	405	97	143	446	473	4.4	71.2	31.6	240	0.57	8.66
85	75	192	617	55	159	637	647	3.0	69.3	36.3	319	0.76	17.85
86	70	178	548	58	144	735	671	4.7	71.1	32.0	321	0.64	16.36
87	82	182	683	65	176	550	669	6.9	68.6	38.1	337	0.76	16.87
88	81	104	479	84	123	651	639	4.9	66.6	29.6	304	0.76	9.75
89	70	103	481	84	124	658	641	4.9	69.8	29.6	305	0.66	9.70
90	224	175	510	77	130	486	570	4.6	40.0	34.1	281	1.68	13.14
91	218	114	501	90	142	645	655	3.6	43.5	29.9	315	1.92	10.07
92	211	102	443	69	98	560	442	-3.9	35.9	37.5	222	1.88	9.07
93	213	134	297	62	66	800	520	-5.2	37.0	23.8	234	1.74	10.92
94	152	113	233	45	43	547	446	1.6	40.8	22.3	197	1.56	11.66
95	84	189	78	0	8	155	120	-0.2	24.9	28.1	52	0.82	18.50
96	65	156	286	22	37	152	178	-1.9	44.1	55.7	96	0.68	16.38
97	72	163	225	19	6	148	180	2.7	39.3	48.2	88	0.65	14.66
98	102	210	268	29	69	167	219	2.7	37.8	43.3	116	0.86	17.73
99	63	149	309	24	59	195	240	2.3	51.4	46.4	125	0.59	13.90
100	67	330	272	18	50	109	191	5.4	44.6	50.3	102	0.59	28.88
101	96	185	366	16	37	183	261	3.5	42.4	51.8	133	0.88	16.94
102	75	188	310	36	81	163	199	-1.7	44.9	51.1	114	0.65	16.45
103	92	148	305	24	65	195	236	1.3	41.7	46.2	124	0.86	13.83
104	101	315	391	29	72	120	247	4.9	41.8	53.8	136	0.88	27.54
105	81	207	343	48	106	150	203	-1.9	44.9	52.3	123	0.70	18.07

CODE	RUN NO.	CATA LYST	REACT TEMP °C	INLET FLOWS (M/MIN) XYL 6 ×10	OXY 5 10	NIT 5 10	GAS ANALYSIS CO2 %	OXY %
DA	106	1C	399	210	266	714	2.30	22.5
K	107	1C	399	172	189	630	3.46	13.4
K	108	1C	399	47	177	887	0.88	15.3
K	109	1C	411	181	242	910	2.68	16.2
K	110	1C	399	110	215	807	1.72	18.5
K	111	1C	399	172	344	752	1.19	27.9
K	112	1C	399	106	191	719	1.33	18.6
K	113	1C	399	89	194	731	1.36	18.4
K	114	1C	399	40	189	788	0.61	18.4
K	115	1C	399	55	171	760	1.23	16.6
K	116	1C	399	88	197	741	1.25	18.7
K	117	1C	399	89	285	701	1.08	26.6
K	118	1C	432	38	166	625	2.53	17.7
K	119	1C	432	44	148	558	2.94	17.2
K	120	1C	391	36	154	580	1.00	19.5
K	121	1C	391	26	149	562	1.08	19.5
-	122	1C	348	132	226	852	0.50	20.1
-	123	1C	366	78	169	636	0.72	19.8

RUN NO.	OUTLET FLOWS XYL	OXY	PA	PI	TOL	CO2	H2O	CO	CONV	SCTY	RATE	P XYL	P OXY
	MOLES PER MIN.							%	%	%	M/GHR	ATM.	ATM.
	6 ×10	5 10	7 10	7 10	7 10	6 10	6 10				5 10	2 10	2 10
106	132	221	298	53	63	232	287	3.4	36.9	38.5	145	1.31	21.58
107	86	135	326	59	100	360	309	-4.1	50.1	37.7	162	0.83	12.97
108	24	163	97	17	21	94	82	-4.8	48.6	42.3	43	0.23	15.21
109	85	185	418	62	81	316	347	0.4	53.2	43.4	181	0.72	15.76
110	64	168	159	53	68	177	151	-4.6	41.3	35.2	85	0.62	18.20
111	88	305	459	35	82	134	289	6.1	49.2	54.1	159	0.78	27.15
112	61	168	227	40	55	123	147	-2.1	42.8	50.1	85	0.66	18.26
113	45	170	187	34	42	127	155	1.9	49.4	42.6	82	0.48	18.12
114	24	180	77	11	20	60	55	-4.9	40.9	47.3	31	0.24	18.33
115	24	154	99	47	52	115	97	-7.1	55.4	32.7	57	0.26	16.44
116	48	175	196	26	30	118	141	0.1	45.3	48.9	75	0.51	18.41
117	45	262	162	39	47	108	155	6.0	49.2	37.2	82	0.45	26.17
118	10	139	15	0	23	202	131	-1.3	74.9	5.1	54	0.12	17.44
119	11	120	40	12	28	210	140	-3.6	74.1	12.1	61	0.16	16.63
120	18	143	55	13	32	74	62	-3.8	49.2	30.8	33	0.25	19.38
121	9	138	53	0	37	77	59	-6.5	64.2	31.5	32	0.13	19.37
122	123	219	19	4	16	58	35	-1.4	7.0	20.6	17	1.13	20.89
123	65	160	22	0	24	55	49	1.4	16.2	17.7	23	0.80	19.68

APPENDIX 3

(a) Effect of Materials of Construction and (b) Rotational Speed

(a)

Run No.	Code	PA collected gms/30 mins	Outlet O_2 %	Outlet CO_2 %
14	N	0.107	18.0	1.90
	ST	0.110	18.0	1.88
	Ni	0.112	18.9	1.88
	ST,Ni	0.108	17.9	1.92

N = Normal Run

ST = Steel added to basket

Ni = Additional Nickel wound round basket

(b)

Run No.	Sample	R.P.M.	PA gms/30mins	Outlet O_2 %	Outlet CO_2 %
15	1	2000	0.137	12.2	2.70
	2	3800	0.141	12.2	2.74
19	1	3800	0.104	17.5	2.28
	2	2000	0.099	17.4	2.22
64	1	2000	0.138	15.7	3.91
	2	3800	0.135	15.6	3.85
65	1	3800	0.132	15.3	4.10
	2	2000	0.129	15.3	4.07

APPENDIX 4

The Fixed-Bed Reactor Results

The results of the thirty-two fixed-bed runs during which product collection were made are contained in this section.

In all runs the catalyst loading consisted of 60.7 gms. diluted with three times its volume of alundum spheres.

The fluid-bed runs were all performed after fixed-bed run 23; on subsequent return to the fixed-bed mode direct injection of o-xylene was employed in the remainder of the fixed-bed runs as it was on all the fluid-bed runs.

RUN NO.	WALL TEMP	INLET FLOWS XYL	OXY	NIT	GAS ANALYSIS XYL	CO2	OXY
	°C	MOLES/MIN			%	%	%
		$\times 10^5$	10^4	10^4			
FXB							
1	427	184	507	1908	0.76	1.5	17.8
2	420	199	473	1780	0.88	1.5	17.5
3	467	210	468	1760	0.94	2.5	16.5
4	484	210	468	1760	0.94	3.1	15.9
5	484	211	467	1757	0.95	3.1	15.9
6	408	215	468	1760	0.97	1.9	17.5
7	483	206	468	1760	0.92	2.5	16.5
8	420	194	468	1760	0.87	1.6	17.6
9	390	212	468	1760	0.95	2.1	17.4
10	370	212	468	1760	0.95	1.4	18.1
11	432	206	468	1760	0.92	2.5	17.0
12	443	202	468	1760	0.91	2.4	17.4
13	446	112	449	1691	0.52	1.6	18.5
14	470	110	453	1705	0.51	1.5	18.6
15	380	116	450	1691	0.54	0.4	20.3
16	416	126	483	1817	0.55	1.6	18.2
17	426	137	518	1949	0.56	1.9	18.2
18	432	97	223	840	0.92	3.2	15.5
19	461	101	224	843	0.95	4.2	14.7
20	403	97	223	840	0.92	2.7	16.5
21	375	97	223	840	0.92	1.3	19.4
22	421	98	264	995	0.78	2.9	16.3
23	472	92	237	891	0.82	4.3	14.8
24	420	388	954	3591	0.85	1.7	17.6
25	455	388	969	3645	0.84	2.5	16.6
26	416	388	980	3681	0.83	1.9	17.4
27	415	388	546	3787	0.90	2.1	8.4
28	423	388	1711	2658	0.89	2.9	34.5
29	413	388	1630	6134	0.50	0.7	19.7
30	440	194	950	3573	0.43	1.1	18.9
31	411	194	955	3591	0.43	0.9	19.2
32	411	194	477	1796	0.85	1.5	17.6

RUN NO.	OUTLET FLOWS XYL	OXY	PA	CO2	H2O	CO	CONV	SCTY	RATE	OUTLET P XYL	OUTLET P OXY
	MOLES PER MIN.					%	%	%	M/GHR	ATM.	ATM.
	$x10^{5}$	10^{4}	10^{5}	10^{5}	10^{5}					10^{2}	10^{2}
FXB											
1	35	425	95	366	554	4.4	80.9	63.8	147	0.14	17.40
2	40	390	105	343	582	5.4	79.7	66.1	157	0.18	17.05
3	49	363	81	577	641	3.5	76.6	50.5	159	0.22	16.03
4	49	350	61	696	681	6.0	76.6	37.9	159	0.22	15.42
5	41	348	79	712	695	1.2	80.8	37.5	169	0.18	15.41
6	67	384	100	432	540	-2.9	68.8	67.8	147	0.30	17.08
7	54	364	67	578	626	6.1	74.0	44.3	151	0.24	16.04
8	44	388	99	352	549	3.4	77.1	66.2	148	0.20	17.18
9	64	382	100	484	541	-5.8	69.7	67.5	147	0.29	16.98
10	101	402	64	314	431	4.1	52.6	57.1	111	0.45	17.78
11	60	374	84	575	562	-4.7	70.8	57.3	144	0.27	16.58
12	67	382	84	540	507	-8.2	66.9	62.3	134	0.30	17.01
13	30	393	34	352	325	-1.2	73.4	41.6	81	0.14	18.21
14	38	399	28	336	306	1.9	65.7	39.1	72	0.17	18.34
15	103	436	TR	88	69	2.4	11.8	TR	14	0.48	20.24
16	24	415	45	372	409	5.7	80.7	44.5	100	0.10	17.88
17	33	444	45	483	414	-4.4	75.3	43.2	102	0.14	17.87
18	11	162	37	347	361	7.1	89.2	42.2	86	0.10	14.98
19	17	154	22	452	379	6.2	83.1	25.7	84	0.16	14.95
20	18	173	44	291	308	-1.5	81.4	55.9	78	0.17	16.03
21	83	206	TR	136	72	-2.5	15.0	TR	14	0.77	19.27
22	18	203	26	371	348	7.7	81.7	32.7	79	0.14	15.86
23	10	164	17	491	379	4.7	89.1	20.2	81	0.09	14.33
24	103	794	178	771	1065	2.6	73.2	62.5	281	0.23	17.23
25	54	755	174	1148	1323	4.3	86.2	52.1	331	0.11	16.12
26	79	802	195	876	1155	1.1	79.7	63.2	306	0.17	17.00
27	69	360	192	937	1208	2.4	82.1	60.3	315	0.16	8.18
28	55	1484	154	1286	1357	4.6	85.9	46.4	329	0.12	33.42
29	61	1521	105	527	661	0.9	44.9	60.2	172	0.27	19.58
30	28	851	95	490	641	5.1	85.7	57.2	164	0.06	18.60
31	37	867	100	400	585	3.7	80.9	63.6	155	0.08	18.96
32	42	395	97	354	563	5.1	78.1	64.3	150	0.18	17.15

NOTES: TR=TRACE
ONLY TRACES OF TOLUALDEHYDE & PHTHALIDE WERE FOUND

APPENDIX 5

The Fluid-Bed Reactor Results

In all of the 15 runs performed after catalyst activation, the catalyst loading was 250 gms.

RUN NO.	TEMP	INLET FLOWS. XYL	OXY	NIT	GAS ANALYSIS XYL	CO2	OXY
	°C	MOLES/MIN			%	%	%
		5 ×10	4 10	4 10			
FLB							
1	401	388	856	3222	0.94	0.8	18.9
2	430	388	951	3580	0.85	1.3	18.2
3	448	388	961	3616	0.84	1.5	18.0
4	470	388	934	3520	0.86	1.9	17.5
5	504	388	942	3544	0.86	2.6	16.8
6	511	388	931	3502	0.87	2.8	16.1
7	520	388	978	3680	0.83	3.0	15.6
8	433	388	931	3502	0.87	1.6	18.0
9	440	970	957	3603	1.7	3.7	14.7
10	434	194	948	3568	0.43	0.7	19.6
11	410	194	963	3621	0.42	0.4	20.0
12	422	970	937	3526	2.1	2.6	15.8
13	415	388	947	3561	0.85	1.1	18.7
14	418	388	1724	2551	0.90	1.1	38.1
15	419	388	546	3917	0.86	0.9	10.1

RUN NO.	OUTLET FLOWS XYL	OXY	PA	PI	CO2	H2O	CO	CV	ST	R	P XYL	P OXY
	MOLES PER MIN						%	%	% M/GHR		ATM.	ATM.
	5 x10	4 10	5 10	5 10	4 10	4 10					2 10	2 10
FLB												
1	247	773	67	5	35	55	6.3	36	48	34	0.60	18.7
2	169	822	116	7	61	84	5.1	57	53	53	0.37	17.9
3	150	817	119	7	67	93	7.1	61	50	57	0.32	17.6
4	109	770	151	10	84	106	3.2	72	54	67	0.24	17.0
5	64	730	155	5	116	129	4.4	83	48	78	0.14	16.0
6	61	706	137	5	126	134	7.1	84	42	79	0.13	15.6
7	43	721	104	4	143	151	1.5	89	30	83	0.09	15.8
8	180	796	96	6	72	83	4.2	54	46	50	0.40	17.7
9	553	664	171	9	173	171	2.1	43	41	100	1.18	14.1
10	82	881	57	4	33	43	4.7	58	51	27	0.18	19.4
11	123	918	31	2	20	29	6.1	37	44	17	0.27	19.9
12	602	705	172	11	118	145	3.6	38	47	88	1.31	15.3
13	208	840	93	5	49	69	5.1	46	52	43	0.46	18.4
14	227	1624	81	4	49	63	3.9	42	50	39	0.52	37.5
15	225	452	88	5	42	62	4.4	42	54	39	0.50	10.0